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February 14, 2005

Mr. Tien Q. Duong
5G-030, EE-32
Forrestal Building
U.S. Department of Energy
Washington D.C. 20585

Dear Tien:

Here is the first-quarter FY 2005 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from <http://berc.lbl.gov/BATT/BATT.html>.

Sincerely,

Frank McLarnon
Manager
BATT Program

cc:	J. Barnes	DOE/OFCVT
	D. Howell	DOE/OFCVT
	E. Wall	DOE/OFCVT
	K. Abbott	DOE-BSO

LBID-2563 (1)

BATT TASK 1 CELL DEVELOPMENT

TASK STATUS REPORT

PI, INSTITUTION: V. Battaglia, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Cell Fabrication and Testing

SYSTEMS: Graphite/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (high-energy, high-voltage Li-ion), Graphite/LiFePO₄ (low-cost Li-ion), and Graphite/LiMn₂O₄ (high-power Li-ion)

BARRIERS: Li-ion systems meeting performance, abuse, and life targets.

OBJECTIVES: The primary objective is to establish a test vehicle for the evaluation of new materials for high-power or high energy, low-cost Li-ion cells.

APPROACH: The testing of novel materials in a standard cell with preset protocols will provide the necessary link between the invention of novel battery components and the diagnostic evaluation of failure modes, and will accelerate the development of EV's, HEV's and FCEV's. Novel components will be developed in BATT Program Tasks 2, 3, and 4 (anodes, electrolytes, and cathodes) for baseline cell chemistries. These components are incorporated into a standardized cell, and then tested using a consistent protocol to determine cell capacity, energy, power, and lifetime characteristics. Tested cell components are then delivered to appropriate investigators involved with BATT Program diagnostic projects.

STATUS OCT. 1, 2004: Further benchmarking of the low-cost Li-ion baseline cell including high-temperature aging will be carried out with larger cell sets to demonstrate reproducibility. Diagnostic analysis of cell components from this study will be combined with those from previous cells to lend insight into the degradation mechanism occurring on the natural graphite electrode in the presence of LiFePO₄.

EXPECTED STATUS SEPT. 30, 2005: Performance measurements on the candidate sources of LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ will be carried out and compared to the baseline material from Seimi. Room temperature benchmarking of this baseline chemistry will be completed. In addition, half-cell studies of LiMn₂O₄ in LiBOB-containing electrolyte for the high-power baseline cell will be carried out. Pouch cells from HQ will be benchmarked with regard to performance and aging and distributed to the diagnostic projects for analysis. Electrodes and cells will be prepared and tested in support of modeling and synthesis projects for the various baseline systems.

RELEVANT USABC GOALS: Specific power 780 W/L, 15 year life, < 23% power fade.

MILESTONE:

- | | | |
|-----|---|------|
| (a) | Test 6 LiFePO ₄ pouch cells from HQ | 3/05 |
| (b) | Benchmark LiMn ₂ O ₄ in LiBOB and LiPF ₆ based electrolyte | 6/05 |

PROGRESS TOWARD MILESTONES

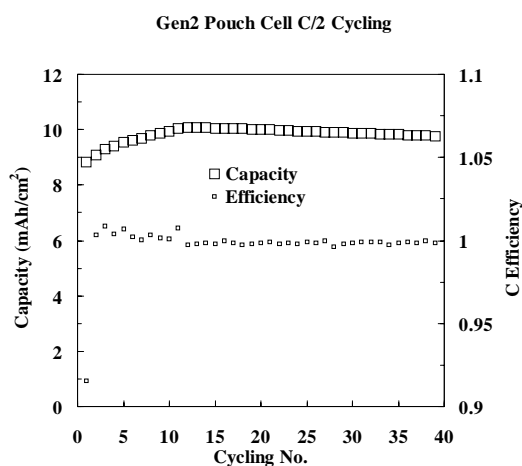
Progress toward milestones

Modifications to Milestones - Since the AOP was written, there have been some modifications to the expected progress and milestones.

Progress toward altered milestones

Milestone 1 - The start of this last quarter saw the departure of the Cell Analysis PI from LBNL and the loss of the post-doc to another research group. The cell making lineage was severely disrupted. Also, a specific recommendation from the last BATT review was to change the emphasis of the program from investigating energy limitations to power limitations. Cells with good rate capability are inherently more difficult to make than cells with high capacity. The combination of these circumstances required a reassessment of the cell making capabilities. With some knowledge of how cells used to be made, the group spent the last quarter re-organizing the laboratory and re-developing its cell making capability with an emphasis on making power cells.

As a result of this effort, the lab is physically in a much better position for making cells sensitive to loss of power. The electrode components are combined in a glove box and will be mixed in an Argon atmosphere. The laminates are dried in one hour as opposed to 24 hours as previously prepared. The laminates are calendared, cut, and tabbed in ~ one hour in the open atmosphere before they are vacuum dried at 60°C for 6 hours prior to returning to a glove box for cell assembly, pouch sealing, and electrolyte filling. The cell's energy cycling appears to be very good, as seen in the graph. The electrolyte vacuum filling remains to be optimized.



LiFePO₄ Base Line (HQ cathode):

More LiFePO₄/graphite cells were received from K. Zaghbi at Hydro-Québec, IREQ (HQ). The cells need to be tested under pressure. A test fixture capable of dialing in a pressure needed to be developed. The fixture is now ready and we intend to test the cells in the next quarter.

Work in the previous quarter indicated that cells made in the lab with this baseline suffered from large contact resistances between the cathode laminate and the aluminum current collector. In anticipation of this problem we developed a methodology for applying a carbon coating on the current collector. Coherent

coatings as thin as 2 µm are now possible.

Milestone 2 - LiMn₂O₄ Baseline (Toda cathode):

Preliminary work in the spinel system has simply focused on making good electrodes. Since performance improvements were seen for both the 3 1/3's material and the LiFePO₄ system from coating the electrode with carbon, we are looking at this effect on this system. Cells with and without carbon coating on current collectors from two different sources with and without calendaring are being made. These cells will be tested for performance with samples sent to Prof. Sastry for contact resistance analysis.

Other progress - LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ Baseline (Seimi cathode):

Seimi paid a visit to us in October. We shared with them some preliminary data of cells with high contact resistance. They sent us their latest material underdevelopment. We will test it based on level of priority.

TASK STATUS REPORT

PI, INSTITUTION: T.J. Richardson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Materials Characterization, Overcharge Protection, Cathode Development

SYSTEMS: High-voltage, high-power: Gr/LiBOB+gBL:EA/LiMn₂O₄
Low-voltage, high-stability: Gr/LiPF₆+EC:DEC/LiFePO₄

BARRIER: Short lifetimes, poor abuse tolerance

OBJECTIVES: Support cell development and diagnostics tasks through structural characterization of active electrode components before, during, and after cycling. Protect cells against degradation and failure due to overcharging by means of lightweight, inexpensive protection mechanisms. Investigate particle isolation and oxygen loss mechanisms in composite electrodes. Synthesize and evaluate alternative electrode materials.

APPROACH: Address primary causes of power and capacity fading by correlating them with changes in the composition and structure of active materials and composite electrodes. Techniques employed include x-ray diffraction (XRD), vibrational spectroscopy, and electroanalytical testing. Continue to develop a reversible overcharge protection mechanism based on components that automatically short overcharged cells. Discover improved cell systems through a limited program of synthesis and evaluation.

STATUS OCT. 1, 2004: Composition and structural analyses of BATT Task 1.1 electrodes have contributed to our understanding of failure and degradation modes in the baseline systems. Electroactive conducting polymers capable of providing overcharge protection in lithium ion cells with cathode potentials above 4.0 V have been characterized. New cathode materials were synthesized and evaluated for introduction into BATT chemistries.

EXPECTED STATUS SEPT. 30, 2005: Improvements in chemistry, morphology and distribution of highly conducting polymers will permit protection of high-power cells against overcharging at rates as high as 3C. High-rate electrode materials will have been characterized for stability and compatibility with electrolytes.

RELEVANT USABC GOALS: Abuse tolerance to cell overcharge and short circuit, 30 ohm-cm² area-specific impedance.

MILESTONE:

Protect LiMn₂O₄ cells against 10 cycles of 5% overcharge at 3C or higher. (July 2005)

PROGRESS TOWARD MILESTONE

The recently developed bilayer configuration with a high voltage polymer on a fibrous Viledon membrane and a lower voltage polymer on a Celgard membrane was applied to lithium cells with spinel-type $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ cathodes. A cell with polymer protection was overcharged by 20% at 4.3 V (Fig. 1a). An unprotected cell was charged to 4.3 V at the same current density (Fig. 1b), and then held at 4.3 V for the same charging time as the protected cell. The protected cell carried the constant current during normal charging and overcharging in each cycle, while the current through the unprotected cell decreased during overcharging. Rapid capacity fading occurred in the unprotected cell, while the protected cell maintained its discharge capacity (Fig. 2). The polymer composites set an upper potential limit of about 4.3 V. Reversible protection was achieved at current densities up to 0.75 mA/cm^2 . At higher currents, the potential limit was higher, and gradual capacity fading took place.

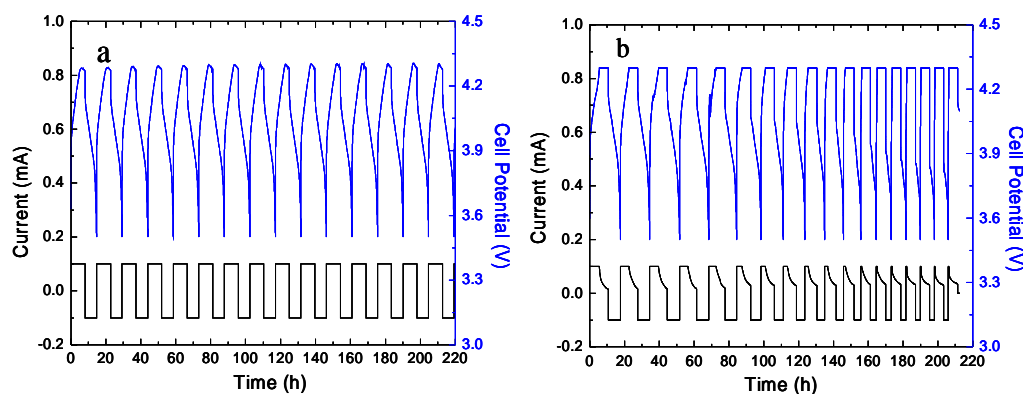


Figure 1

After extensive cycling under above conditions, the cathodes were removed from these cells at the end of charge and examined by X-ray diffraction. The electrode from the protected cell showed no evidence of damage and was in the fully charged state, indicating no self-discharge due to the protection mechanism. On the other hand, the XRD pattern of the cathode from the unprotected cell showed significant peak broadening and a shift to a smaller unit cell, consistent with our previous FTIR study, which suggested conversion to a defect spinel by Mn dissolution.

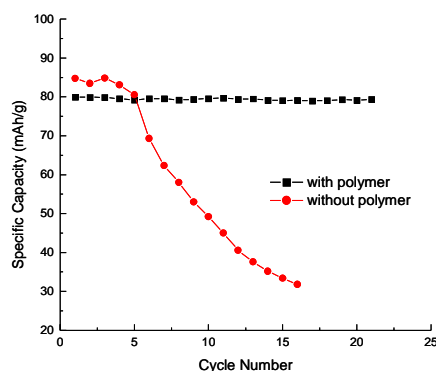


Figure 2

TASK STATUS REPORT

PI, INSTITUTION: K. Zaghib, Hydro-Québec (IREQ)

TASK TITLE - PROJECT: Cell Development - Lithium-Ion Polymer Batteries with Low-Cost Materials

SYSTEMS: Low-cost Li-ion

BARRIER: High cost of Li-ion batteries

OBJECTIVES: Fabricate Li-ion/polymer cells (4 cm^2 area) using cell chemistries proposed by DOE, and send 50% of the total cells to LBNL for testing. Optimize gel formation as a function of the % plasticizer content, optimize the thermal cross-linked temperature by using new polymer with ionic liquid or liquid electrolyte as plasticizer. Determine the conductivity of gel electrolyte as a function of plasticizer content in particular at low temperature. Study the interface of gel electrolyte in contact with the active materials in electrodes.

APPROACH: Our approach is to synthesize and coat electrodes (both anode and cathode) with low-cost materials, and to evaluate these materials in Li-ion/polymer cells. Additional work will focus on gel polymers, as well as studies to identify an appropriate salt and solvent to increase the performance and charge/discharge rate of Li cells at low temperatures. The gel electrolyte will be compared to a liquid electrolyte (100%) by measurements in half cells and Li-ion polymer cells at low temperatures.

STATUS OCT. 1, 2004: We will optimize the composition of anode (natural graphite, fibers) and cathode materials in the electrodes as a function of the water-soluble binder (WSB) (no fluoride), with the goal of reducing the amount of binder by 50% compared to standard electrodes with PVDF. To reduce the amount of binder and the cost of the coating, we will demonstrate a new coating process using WSB in the anode and cathode (LiFePO_4). Also, we expect to show the effect the soluble WSB on other baselines chemistries (LiMn_2O_4 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$). A study of the effects of PVDF and WSB in electrodes to improve the safety aspect of the battery will be completed. We expect to provide primary cycling data (including PNGV protocol) from Li-ion/polymer cells containing WSB and a low-cost Li salt. We will continue to develop LiFePO_4 (Phostech)-coated carbon with higher tap density.

EXPECTED STATUS SEPT. 30, 2005: We will determine the composition of gel electrolytes, which are based on a new high-viscosity polyether gel, as a function of the amount of ionic liquid (molten salt) or liquid electrolyte used as plasticizers. These plasticizers should be beneficial in reducing the amount of polymer and to increase the safety of the cell, and will be compared to results obtained with electrodes containing PVDF and WSB. We will optimize the gel electrolyte with different anodes based on hard carbon, soft carbon and graphite to select a good candidate for low-temperature and high-rate applications. The content of cathode material and gel electrolyte will be optimized to increase the high-rate performance of LiFePO_4 , and other baselines chemistries (LiMn_2O_4 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$). ARC safety test using a new gel electrolyte in contact with anodes and cathodes will be evaluated in collaboration with J. Dahn. We expect to provide cycling data, including the PNGV protocol, in Li-ion polymer cells that contain gel electrolyte based on polymer-ionic liquid, polymer-liquid electrolyte and 100% liquid electrolyte.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10-year life, < 20% capacity fade.

MILESTONES: 1) Identify an ionic liquid with low-cost, high-viscosity polymer (April 2005). 2) Deliver thirty (30) cells to LBNL (10 cell every four months). 3) Produce LiFePO_4 with high tap density at Phostech. (February 2005).

PROGRESS TOWARD MILESTONE

We will complete studies of WSB in coating of LiFePO_4 and natural graphite. Optimizing *in situ* gel formation as a function of % liquid content and thermal cross-linked temperature will continue. We will measure the ionic conductivity of the gel containing a viscous electrolyte based on GBL, EC and PC, which will increase the ionic conductivity at low temperature. The wettability of both the natural graphite anode and LiFePO_4 cathode will be investigated by impedance spectroscopy and SEM.

To reduce the amount of polymer and the cost of the coating, we will use a new process with gel electrolytes based on ionic liquids (propyl-methyl-imidazolium TFSI and hexyl-methyl-imidazolium TFSI).

Also, we expect to investigate the effect of the gel electrolyte on other baseline chemistries (LiMn_2O_4 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$). We will determine the composition of the anode (soft and hard carbons) and cathode material as a function of the content of gel electrolyte.

Our collaboration with LBNL researchers (Battaglia, Kostecki) who are working on BATT baseline chemistries will continue. Hydro-Québec will fabricate LiFePO_4 cathodes with WSB and other BATT baseline chemistries (LiMn_2O_4 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$). These electrodes will be sent to LBNL for interfacial studies and Raman spectroscopy characterization.

A coating with gel electrolyte will be sent to Kerr (LBNL) for evaluation. Collaborations will be established with other groups (Creager and Smith) in the BATT Program to select the appropriate crosslink agent, amount of plasticizer and additives to obtain better electrochemical performance at low temperature.

Efforts will continue to fabricate 30 Li-ion gel-electrolyte cells containing LiFePO_4 and other BATT baseline chemistries (LiMn_2O_4 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$) for evaluation by LBNL. Similar types of cells will also be evaluated at Hydro-Québec.

TASK STATUS REPORT

PI, INSTITUTION: D. Wheeler and J. Harb, Brigham Young University

TASK TITLE – PROJECT: Design, Optimization, and Fabrication of Li-ion Electrodes for High Power Applications

SYSTEM: Low-voltage, high-stability: Gr/LiPF₆+EC:DEC/LiFePO₄

BARRIERS: Electrode impedance that limits power density and cycle life

OBJECTIVES: Improve battery power and life through novel electrode structures. Increase understanding of how electrode morphology influences performance. Develop tools to analyze high-rate performance of electrolytes.

APPROACH: We will explore methods for maximizing the high-power performance of low-cost LiFePO₄ composite cathodes. Our efforts will include the use of a variety of different electronically conductive additives in order to improve high-rate performance and diminish capacity fade due to loss of conductivity/connectivity. Electrode structure will also be optimized to enhance performance. In addition, as part of our efforts to optimize electronic and ionic conduction in composite electrodes, we will conduct Hall-effect experiments and molecular dynamics (MD) simulations in order to determine transport properties for liquid electrolytes.

STATUS OCT. 1, 2004: This will be our first month of the new project. We will acquire the materials required to begin fabrication and testing of LiFePO₄ cathodes. Initial efforts will also include work on the construction of an apparatus for Hall-effect experiments. An improved set of *ab initio* based potentials for MD simulations will be developed.

EXPECTED STATUS SEPT. 30, 2005: We will have demonstrated the power and cycle-life improvements possible with different types of electronically conductive additives in LiFePO₄ cathodes, and identified the factors that limit performance. Processing steps for the mixing and application of improved cathode slurries will also have been demonstrated. We will have shown proof-of-concept results for obtaining the electrolyte transference number using the Hall Effect. MD simulations of the transport properties of LiPF₆ in liquid carbonate electrolytes, as a function of temperature and concentration, will be completed.

RELEVANT USABC GOALS: HEV-related goals of 30 $\Omega\text{-cm}^2$ impedance and 300k cycles

MILESTONES:

- (a) Demonstrate that Hall Effect can be used to measure transference numbers. (Apr. 2005)
- (b) Complete initial investigation toward optimizing LiFePO₄ cathode. (Aug. 2005)

PROGRESS TOWARD MILESTONES

Efforts in this, our first quarter on this project, included the establishment of fabrication and test procedures for the LiFePO_4 chemistry, setting up a new dry box (purchased with BYU funds), moving our labs to an updated facility, the training of two new graduate students, and the acquisition of battery materials for future use. A detailed investigation of the impact of the composite electrode structure on the performance of doped spinel electrodes, initiated prior to the BATT project, was also continued this quarter under BATT funding. The results of this investigation will guide our efforts to enhance the power performance and cycle life of the cathode as we transition to chemistries of interest in the current program.

Cells utilizing LiFePO_4 cathodes fabricated by Hydro-Québec and a lithium counter electrode were assembled and tested. The observed cell capacities and voltage profiles were similar to those reported by Striebel group. The performance of cathodes we fabricated from Hydro-Québec-supplied active material was also comparable, although the theoretical capacity of these cells was about 30% lower as our casting procedure resulted in less active material per area. This issue will be addressed during the next quarter.

The detailed investigation of the spinel electrodes seeks to explain the observed positive impact of carbon-nanotube additive on cathode performance. While it is understood that nanotubes do not currently represent an economically viable option for use as the conductive filler for vehicle batteries, an understanding of the physical mechanisms which lead to improved performance will guide our choice of viable electrode materials and fabrication methods. The optimal mass fraction of conductive fiber filler for high-power performance exceeds the amount required for electrical resistivity across the whole electrode to be negligible. This appears to indicate that contact resistance between the active-material particles and electrically conductive network is a significant effect. Through additional experimentation and modeling we will investigate this effect.

We are still evaluating the feasibility of using the Hall Effect to determine directly the cation transference number for battery electrolytes. While a precedent does exist for the measurement of the Hall Effect in liquid electrolytes (P. Gérard et al., *J. Electrochem. Soc.* **137**, 3873 (1990)), earlier researchers have argued that their experimental results indicate anisotropic transport properties in the presence of a strong magnetic field; they hypothesize that the mobilities of the ions differ between electric-field and Lorentz driving forces. We are currently constructing a Hall-effect apparatus in order to test this hypothesis and assess the viability of the technique.

BATT TASK 2 ANODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Anodes - Non-Carbonaceous Materials

SYSTEMS: Graphite/LiPF₆+EC:DEC/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂
Graphite/LiBOB+gBL:EA/LiMn₂O₄

BARRIER: Cost, low temperature- and abuse tolerance limitations of Li-ion batteries

OBJECTIVES: To replace graphite with an alternative inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. The project addresses the need to improve irreversible capacity losses of intermetallic electrodes as well as the low temperature operation and abuse tolerance of Li-ion cells.

APPROACH: Our approach over the past few years has been to search for inexpensive intermetallic electrodes (primarily for EV applications) that provide an electrochemical potential a few hundred mV above the potential of metallic Li, and a capacity of 300 mAh/g and ~2000 mAh/ml. We will focus on: 1) matrix reactions that, when combined with insertion reactions, may have a stronger chance of success than when topotactic reactions are used alone; 2) composite electrodes with Al-, Si-, Sn-, and Sb components to determine their rate capability; 3) pre-lithiation reactions to fabricate charged electrodes for use against non-lithiated metal oxide electrodes and to overcome first-cycle irreversible capacity loss; 4) couple low potential metal oxide negative electrodes against the high-potential layered and spinel cathodes of Task 4.1 to yield high-rate and abuse-tolerant Li-ion cells (>3 V) for HEV applications.

STATUS OCT. 1, 2004: Composite electrodes containing graphite and a metal component such as Sn or Sb delivered the targeted capacity milestone of 300 mAh/g for 100 cycles. Although in some instances an irreversible capacity loss <20% was achieved on the first cycle, this capacity loss was still a limiting parameter in most cells. Efforts to find a high performance, low potential (<1 V vs. Li⁰) metal oxide anode were unsuccessful. Several Li_{1+y}MX₂ reactions (e.g., M=V, Mn, Ni, Co) were modeled by *ab initio* calculations; theoretical predictions were verified by experimental observations. Studies of SEI layers on intermetallic electrodes were in progress.

EXPECTED STATUS SEPT. 30, 2005: The low temperature behavior and rate capability of carbon/metal (intermetallic) electrodes will have been determined. The first-cycle irreversible capacity loss of the electrodes and their capacity retention on cycling will have been improved.

RELEVANT USABC GOALS: 10 year life, <20% fade over a 10-year period.

MILESTONES: By September 2005: 1) Carbon/intermetallic electrodes: 5-15% irreversible capacity fade on initial cycle; 300 mAh/g for more than 100 cycles; low temperature rate capability determined. 2) Prelithiated carbon/intermetallic/metal oxide electrodes: synthesized and evaluated electrochemically; 3) Metal oxide electrodes: electrochemical evaluation against high-potential layered and spinel electrodes in >3 V Li-ion cells.

PROGRESS TOWARD MILESTONES

We have initiated studies to determine the rate capability of several intermetallic compounds at various temperatures. The alloys Cu_6Sn_5 and Cu_2Sb were selected for the initial investigations. Lithium reacts with these copper-based compounds by two distinct processes: 1) Li insertion, which is accompanied by partial copper extrusion, to yield a ternary intermediate compound (Li_2CuSn and Li_2CuSb), and 2) additional lithium insertion that leaves an active lithium Zintl phase (Li_{3+x}Sn and Li_3Sb) and extruded nano-grained copper metal. The two processes occur at different potentials. The cycling stability and rate capability of these electrodes is dependent on the selected voltage window, the extent of metal displacement and side reactions with the electrolyte. We also explored the effect of adding conductive additives, such as copper or silver, to the parent electrode matrix.

The Cu_6Sn_5 and Cu_2Sb materials were synthesized by ball-milling and sieved to 10-15 μm size. Additives, such as acetylene black, copper (< 50 μm), or silver (< 50 μm) were added to the electrode at the mixing stage. Lithium half cells were constructed and tested over two different voltage windows (2.0-0 V and 1.2-0.2 V for Cu_6Sn_5 ; 2.0-0 V and 2.0-0.6 V for Cu_2Sb). Capacity data were collected over these potential windows using five different current rates for 10 cycles. Data from the 5th cycle were typically used for the capacity vs. current rate plots in Fig. 1; literature data for graphite electrodes (SFG10) are included for comparison [1].

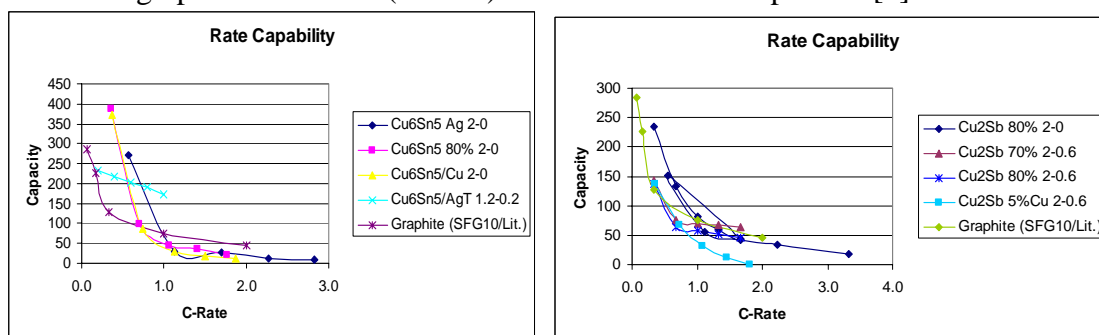


Figure 1. The effect of various conductive additives on the rate performance of Cu_2Sb and Cu_6Sn_5 at room temperature compared to graphite (SFG10).

In general, Cu_6Sn_5 electrodes did not cycle well when cycled over the whole potential window (2.0-0 V), nor did they provide any rate advantage over SFG10. By contrast, Cu_6Sn_5 electrodes with an Ag additive and a smaller voltage window, showed a significantly superior rate capability, at least between a C/10- and a 1C rate. Experiments are continuing. On the other hand, Cu_2Sb electrodes with an AB additive (10-20%) exhibited a slightly superior rate capability than SFG10 when cycled between 2.0 and 0.6 V. The best performance was obtained from a Cu_2Sb (70%), AB (20%), binder (10%) electrode, which delivered approximately 30% higher capacity than SFG10 at a 2C rate. Adding metallic copper or silver to Cu_2Sb was detrimental to electrochemical performance. Work is in progress to monitor the effect of temperature on the rate capability of the electrodes.

We have also initiated studies of stabilized lithium metal powder (SLMP) from FMC Corporation to evaluate its viability as a pre-lithiating agent for intermetallic and metal oxide negative electrodes in order to overcome first-cycle irreversible capacity loss phenomena.

Reference [1]: B. Veeraraghavan et al, J. Electrochem. Soc., **149**, A675 (2002).

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Anodes - Novel Materials

SYSTEMS: Li-Ion: all systems

BARRIER: Cost, safety and volumetric capacity limitations of Li-ion batteries

OBJECTIVES: To replace the presently used carbon anodes with safer materials that will be compatible with low cost manganese oxide and phosphate cathodes and the associated electrolyte.

APPROACH: Our anode approach is to explore, synthesize, characterize and develop inexpensive materials that have a potential around 500 mV above that of pure Li (to minimize risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. We will place emphasis on simple metal alloys/composites, and on intercalating oxides. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal and kinetic stability.

STATUS OCT. 1, 2004: We have shown that vanadium and manganese oxides, in their highest oxidation states, are not prime candidates. Pure Al foil and expanded metal was found to have a high capacity, react readily with Li but its capacity faded rapidly on cycling in carbonate-based electrolytes; Al-based alloys show inferior behavior to pure Al. Tin containing materials, such as MnSn_2 cycle well for a few cycles before capacity fade sets in. Pure tin foil anodes cycle better than pure Al or MnSn_2 , but the cell impedance was found to increase markedly after about ten cycles; an expanded tin grid was marginally superior, but not sufficient to justify further study.

EXPECTED STATUS SEPT. 30, 2005: From our program to understand capacity fade of tin on cycling, we expect to have defined the key parameters determining capacity loss, to have determined the impact of tin morphology on capacity fade, and as a result to have identified several additional non-Al binary alloys; and to have improved the electrochemical performance of the materials identified.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles, and abuse tolerance to cell overcharge and short circuit.

MILESTONES: (a) We will design a program to identify, understand and mitigate the capacity loss on cycling of simple alloy systems. This will result in a milestone to understand and define the key parameters determining capacity fade in pure tin and its alloys by June 2005, and to propose a means of remediating that fade. (b) We will identify the impact of electrolyte solvent and salt on the capacity retention and rate capability of pure tin, including first cycle capacity loss by October 2005.

PROGRESS TOWARD MILESTONES

In the previous quarter, we reported the electrochemistry of tin foil and expanded tin grids, and showed that they had higher capacities than graphite as a host for Li. However, the capacity rapidly decays after 10 to 15 cycles to values comparable to that of graphite.

Earlier research in the BATT program at ANL showed that the intermetallic Cu_6Sn_5 showed attractive anodic behavior for several cycles. We therefore decided to try and stabilize tin foil by binding it to a Cu-support foil through the formation of the above intermetallic just as in solder formation reactions. All the components, the Cu, the Sn and the Cu_6Sn_5 all have excellent electronic conductivity and so no conductive diluent should be needed in the electrode system. The tin-copper foil was prepared mechanically using a rolling machine, to form the triple-layered structure, with a Cu-Sn alloy layer, most possibly Cu_6Sn_5 , sandwiched between a tin layer and a copper layer. The electrochemical cycling at a current density of $1\text{mA}/\text{cm}^2$ between voltage limits of 0 and 1.4 V is shown below in Fig. 1. The voltage plateaus are similar to those of a pure tin anode reacting with Li, as expected for the layer reacting first with the Li. However, a large capacity loss was observed after the first Li insertion, following which the capacity fell to 250mAh/g ; the reason for this is not clear. We are presently attempting to form a fresh clean sample that does not show the large capacity above 0.4 V, which suggests the presence of oxide. This oxide might be formed during the rolling process, where the local temperature may exceed 100°C , which had to be repeated many times to reach the final thickness of $\sim 50\mu\text{m}$. The existence of the oxide affects both the capacity and reversibility as it may separate the tin and copper resulting in a highly resistive interface.

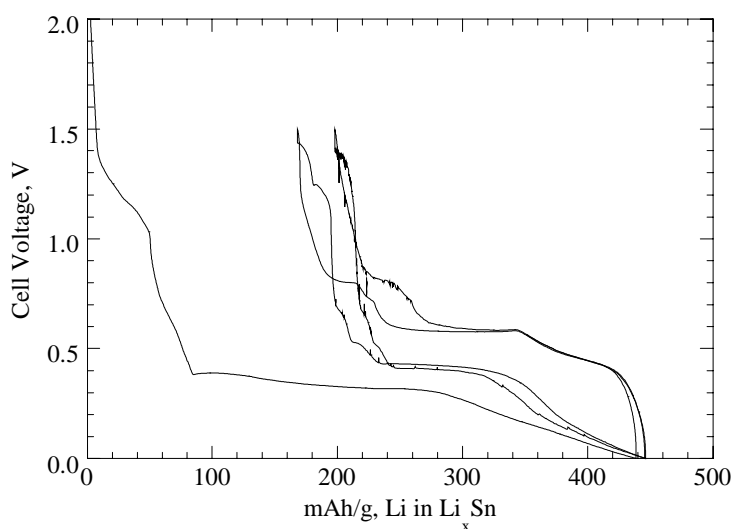


Figure 1. Cycling of the as-prepared Cu-Sn foil at $1\text{mA}/\text{cm}^2$.

Further plans to meet or exceed milestones: None

Reason for changes from original milestones: No changes

Publications and Presentations resulting from the work.

1. Peter Y. Zavalij, Shoufeng Yang, and M. Stanley Whittingham, "Structural Chemistry of New Lithium Bis(Oxalato)Borate Solvates", *Acta Cryst.*, 2004, B60: 716-724.

2. Quan Fan, Peter Y. Zavalij and M. Stanley Whittingham, "Anode Hosts for Lithium Batteries: Revisiting Tin and Aluminum", MRS Meeting, Boston, MA November 30th 2004.

TASK STATUS REPORT

PI, INSTITUTION: G.A. Nazri and D. Curtis, University of Michigan
T. Malinski, Ohio University

TASK TITLE - PROJECT: Anodes – Novel Composite Anodes for Lithium-ion Batteries

SYSTEMS: Low-cost Li-ion battery, improved safety, long cycle and calendar life

BARRIERS: Poor cycle life, poor safety, self-discharge, and electrolyte decomposition

OBJECTIVES: Develop a low-cost and safe composite anode plate with no intrinsic irreversible capacity loss (ICL) and with higher gravimetric and volumetric energy density than the current carbonaceous anodes. Improve the kinetics of the Li insertion-extraction process in the composite anodes for application in high-power Li-ion cells.

APPROACH: Prepare alternative composite anodes *via* reactive mechano-milling of anode materials with lithium or lithium hydride to eliminate inherent irreversible capacity loss of metal-oxide anodes. Form a desirable synthetic SEI layer *via* the mechano-reduction of oxide anodes in presence of electrolyte, and improve kinetics of lithium insertion - extraction process by optimization of anode particle size to nanoscale.

STATUS OCT. 1, 2004: The optimization of mechano-milling process parameters for reactive reduction of metal oxide, nitride and phosphides anodes will be completed. The chemical nature of the SEI formed on metals and alloys after due to reduction of their oxides, nitrides, and phosphides will be completed. An electrochemical study of the composite anode in baseline electrolyte (EC-DMC containing 1M LiPF₆) will be studied.

EXPECTED STATUS SEPT. 30, 2005: Final report will be submitted.

RELEVANT USABC GOALS: Exceeding 10-year life, high power battery electrode, low cost battery and high safety

MILESTONES: Final report will be submitted by June 30, 2005.

BATT TASK 3 ELECTROLYTES

TASK STATUS REPORT

PI, INSTITUTION: N.P. Balsara, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Development and Polymer Electrolytes and Gels for Advanced Lithium Batteries

SYSTEMS: Nanostructured polymer electrolytes based on polystyrene-polyethyleneoxide (PS-PEO) block copolymers. End crosslinked PEO swollen with EC:DEC mixtures.

BARRIERS: Poor electrolyte transport and low power, particularly at low temperatures, short life due to power and capacity fade.

OBJECTIVES:

- Obtain PS-PEO diblock copolymer films with maximum ionic conductivity.
- Study the stability of PS-PEO electrolytes against Li electrodes.
- Develop and characterize the properties of uniformly crosslinked PEO gels swollen with EC:DEC mixtures.

APPROACH: To synthesize and characterize new polymeric electrolytes. This includes gel electrolytes and nanostructured dry polymer electrolytes. Polymers will be characterized by methods such as neutron scattering, dielectric relaxation spectroscopy, rheology and light scattering to obtain new insights into the rate-limiting transport processes. The materials will be tested for stability against Li electrodes.

STATUS OCT. 1, 2004: Rheological properties of PEO/LiTFSI and polytetramethyleneoxide/LiTFSI (PTMO/LiTFSI) mixtures have been measured and analyzed. Polystyrene-polyethyleneoxide (PS-PEO) block copolymers will be synthesized. Low cost synthetic routes for uniformly crosslinked polymer gel electrolytes will be established. The relevant mechanical and electrical properties of the electrolytes will be measured.

EXPECTED STATUS SEPT. 30, 2005: Synthesis and characterization of a new class of gel electrolytes with uniform crosslinking density. Completion of structural and conductivity measurements on the gel electrolytes. Characterization of nanostructured PS-PEO electrolytes including tests of stability against Li electrodes. We will continue collaborating with John Kerr and other members of the BATT program on the thermodynamic and rheological characterization of polymer gel electrolytes.

RELEVANT USABC GOALS: 30 ohm-cm² area-specific impedance, cold cranking capability to -30°C, 300,000 shallow discharge cycles, abuse tolerance to cell overcharge and short circuit.

MILESTONES:

1. To measure conductivity, mechanical properties, and stability against Li electrodes of dry, nanostructured PS-PEO-based electrolytes. (Sept. 2005)
2. Synthesize and characterize uniformly crosslinked PEO systems for gel polymer electrolytes applications. (Sept. 2005)

PROGRESS TOWARD MILESTONES

1. Nanostructured Polymer Electrolytes.

We have measured the electrical, mechanical, and morphological characteristics of a series of a poly(styrene-block-ethylene oxide) diblock copolymer PS-b-PEO systems with varying amounts of added PEO homopolymer. Characterization tools used include small angle X ray scattering (SAXS), transmission electron microscopy (TEM), optical birefringence, and rheology.

Conductivity measurements were made on mixtures doped with small amounts of LiTFSI (EO:Li =50:1). The conductivity of our system increases by a factor of four when the PEO volume fraction in the mixture changes from 0.38 to 0.40. We attribute this to the formation of a continuous network of PEO channels in our system. At 80°C, preliminary indications are that the modulus of this material exceeds the upper limit of our current rheometer (which is at least 10^8 dyn/cm²). Our sample with volume fraction of 0.40 thus has half the ionic conductivity of pure PEO homopolymer but a modulus that is at least two orders of magnitude greater than that of pure PEO.

In an effort to understand the interactions of the Li⁺ ions with the PEO chains, we performed small angle neutron scattering (SANS) experiments on a series of PEO blends with a 19:1 ratio of hydrogenous PEO-to-deuterated PEO with varying levels of Li salts (LiTFSI and LiClO₄). All samples were prepared and sealed in airtight sample holders in the dry box to avoid any moisture contamination. Samples were analyzed for H₂O contamination after the SANS experiments using NMR, and found to be completely dry. We have established that the scattering peaks observed in our previous experiments were the result of water contamination. Our results indicate that the changes in the PEO conformation with increasing Li concentration are less than 8 %.

2. Polymer Gel Electrolytes.

We have begun work on the polymer electrolyte gel system. We are creating crosslinked networks of commercially available polymers/monomers that can be swollen with Li salt solutions in EC/PC/DMC mixtures. Two systems have been identified: (1) poly (acrylamidomethylpropanesulfonic acid) based gels, (2) crosslinked PEO networks.

Acrylamidomethylpropanesulfonic acid is an inexpensive monomer that is widely used in personal care products for its biocompatibility and hydrophilicity. We have experience in making crosslinked networks of poly(AMSA) using crosslinking agents such as N-N'-methylenebis(acrylamide). We will monitor the crosslinking density to control the rheological properties of the poly(AMPSA). The H⁺ in poly(AMPSA) can easily be replaced by Li⁺ using *sec*-butyllithium, to give a single ion conductor.

TASK STATUS REPORT

PI, INSTITUTION: J. Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - R&D for Advanced Lithium Batteries

SYSTEMS: High-voltage, high-energy: Gr/LiPF₆+EC:DEC/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂
Low-voltage, high-stability: Gr/LiPF₆+EC:DEC/LiFePO₄
High-voltage, high-power: Gr/LiBOB+γBL:EA/LiMn₂O₄

BARRIERS: Poor electrolyte transport and low power, particularly at low temperatures, short life due to power and capacity fade, low abuse tolerance.

OBJECTIVES:

- Determine and quantify the improvement (if any) in abuse tolerance of polymer gel electrolytes over liquid electrolytes.
- Determine the limitations on Li-ion transport in polymer gel electrolytes and the electrolyte component of composite electrodes and develop materials capable of high power operation at ambient temperature with lithiated carbons/Li metal alloy anodes and high voltage cathode materials.
- Determine the feasibility of the use of Li metal electrodes with polymer gel electrolytes and provide operating conditions that prevent dendrite growth and high coulombic efficiencies at HEV rates.

APPROACH: A physical organic chemistry approach is taken to electrolyte design, thereby ensuring that not only are the sources of poor performance and failure pinpointed but also the problem can be corrected through materials design and synthesis.

STATUS OCT. 1, 2004: Characterization of mechanical, transport, electrochemical and chemical properties of cross-linked comb-branch and linear polymers and polyelectrolytes will be completed for both dry polymer electrolyte use with Li metal and polymer gel electrolytes with carbon. Modifications of Li metal surfaces and conducting carbon particles will be assessed.

EXPECTED STATUS SEPT. 30, 2005: State-of-the-art polymers will be procured or synthesized to prepare polymer gel electrolytes with the base system electrolyte components. The effects of the gel on abuse tolerance and transport properties will be determined. The performance of single-ion conductor gels will be compared with the binary systems. Compatibility of the polymer electrolyte and polyelectrolyte gels with Li metal and Li alloy electrodes will also be explored.

RELEVANT USABC GOALS: 15 year life, <23% power fade, specific power 625 W/kg at the system level.

MILESTONES:

- 1) Demonstrate and quantify the change in abuse tolerance resulting from use of gel polymer electrolytes relative to liquid electrolytes in the three cell systems. (Sept. 2005)
- 2) Quantify the effect of gel polymer electrolytes on transport properties relative to liquid electrolytes. (Sept. 2005)

PROGRESS TOWARD MILESTONES

1. Abuse Tolerance of Gel Electrolytes.

The chemical reactions of ethylene oxide based polymers and solvent components (EC, EMC) with Lewis acid salts (LiPF_6 , LiBF_4 , LiAsF_6 , LiBoB) have been investigated using GC/MS, GPC and CE. Significant amounts of fluorophosphates species have been detected by GC/MS when LiPF_6 is used as the salt, consistent with the reaction of PF_5 with ethers. The mass spectrum has even revealed the presence of an adduct of PF_5 with ethylene carbonate when the electrolyte is injected neat. The presence of organic groups on the fluorophosphates has also been detected. Some of these organic groups appear to be quite large as judged by the mass spectra. These indicate that large organofluorophosphate anions may be formed due to the Lewis acid chemistry that may have poor transport properties and slow electrode kinetics. Further investigation of this chemistry is underway and the other Lewis acid anions will also be investigated. Analysis of these organofluorophosphate and other acid products requires the development of some new methods.

2. Transport Properties.

Transport property measurements of LiTFSI-ZTP500 polymer electrolytes have been completed for various levels of cross-linking. The diffusion coefficient is reduced by three times by crosslinking. The concentration potentials and hence the transference numbers are unaffected by crosslinking, as expected. The exchange current density and hence the interfacial impedance at lithium metal electrodes is altered by two orders of magnitude by crosslinking the polymer electrolyte. These properties impact the initiation and growth of dendrites. This polymer network will be swollen with solvent in the next quarter to form a gel and the same properties will be measured. The crosslinked polymer electrolyte appears to function better in a composite cathode. The fade rate of V_6O_{13} cells appears to be lower for the crosslinked material. This may indicate better mechanical properties as a binder.

These experiments are carried out to complete work on dry lithium/polymer systems as well as provide a comparison for the gel systems that will be prepared by addition of solvent components to the crosslinked polymers.

3. Mechanical Properties of Polymer Gel Electrolytes.

The mechanical properties of the crosslinked ZTP500 polymer have been measured. The effect on the moduli and transitions will be measured as a function of added solvent. These experiments are in process.

TASK STATUS REPORT

PI, INSTITUTION: S.A. Khan, P.S. Fedkiw, North Carolina State University;
G.L. Baker, Michigan State University

TASK TITLE - PROJECT: Electrolytes - Composite Polymer Electrolytes for Lithium and Lithium-Ion Batteries

SYSTEMS: Low cost composite polymer/gel electrolytes

BARRIER: Short lithium battery lifetimes and high costs.

OBJECTIVES: The ultimate objectives are to develop composite polymer/gel electrolytes that are low-cost, have high conductivities, impart electrode-electrolyte interfacial stability, and yield long cycle life.

APPROACH: Our approach is to use surface-functionalized fumed silica fillers in BATT-baseline and candidate systems to determine the effects of filler type and concentration on interfacial stability and cell cycling. We correlate these electrochemical characteristics with mechanical properties and materials chemistry (*e.g.*, silica-type or PEO-type, synthesized by Baker or Kerr, respectively). Data collected include elastic and viscous moduli, ionic conductivity, transference number, Li cycling efficiency, Li-electrolyte interfacial resistance, and full-cell cycling capacity using 4-V cathodes.

STATUS OCT. 1, 2004: We have established that fumed silica-based composite electrolytes with low-molecular weight (MW) PEOs exhibit desirable mechanical properties characteristic of solid electrolytes (*e.g.*, elastic modulus $G' > 10^5$ Pa), yet have the processability of liquids and display conductivities rivaling liquid electrolytes ($\approx 10^{-3}$ S/cm at 25°C). Fumed silica stabilizes the Li/electrolyte interface, effectively suppresses Li dendrite growth, and attenuates Al corrosion in presence of LiTFSI. We have found that addition of fumed silicas into low-MW PEOs significantly improves charge-discharge cycle performance, coulombic and energy efficiencies, rate capabilities, and self-discharge performance of Li/V₆O₁₃ cells. We have further determined that adding fumed silica improves the rheological properties of both high-MW and mixed-MW polymer electrolytes, but can be either beneficial or detrimental to ion-transport behavior. In this regard, adding fumed silica also improves the interfacial stability of Li/electrolyte (both high-MW and mixed-MW PEO) interface and cycle performance of Li/V₆O₁₃ cells. We have also synthesized single-ion conducting fumed silica [Degussa R711-poly(lithium 2-acrylamido-2-methyl-1-propanesulfonate), R711-pLiAMPS].

EXPECTED STATUS SEPT. 30, 2005: We expand the scope of our work to explore effects of adding fumed silica into BATT baseline electrolytes for Li-ion systems including rheological and transport properties, and interfacial stabilities. We will also examine Li/electrolyte interfacial stability and rheology of electrolytes consisting of mixtures of Li salt + single-ion conducting fumed silicas as a function of electrolyte composition and salt type.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade.

MILESTONES: (a) Investigate effects of adding fumed silica into BATT baseline electrolytes on transport and rheological properties, and interfacial stabilities, with a focus on low-temperature performance. September 2005.

(b) Examine the interfacial stability and rheology of mixtures of Li salt + single-ion conducting fumed silicas in polymer gel solvents as a function of silica concentration and salt type, including new lithium imide salts developed by Drs. DesMarteau and Creager at Clemson. September 2005.

PROGRESS TOWARD MILESTONES

- **Accomplishments toward milestones over last quarter:**

We have begun investigating effects of adding fumed oxides into BATT baseline liquid electrolytes. Two kinds of liquid electrolytes were used: 1M LiPF₆ (lithium hexafluorophosphate) + EC (ethylene carbonate): DEC (diethyl carbonate) (1:1, volume ratio) and 1M LiPF₆ + EC: EMC (ethyl methyl carbonate) (1:1). Three types of fumed oxides were used: aluminum oxides (neutral and weakly acidic), silica oxides (A200 and R805), and aluminum and silica oxide mixture (COX84, 84% SiO₂ + 16% Al₂O₃). Fumed aluminum oxides do not form a gel and sediment. A200, R805 and COX84 form gel electrolytes in the above two liquid electrolytes. We have measured conductivity from -3 to 68°C for these liquid and composite gel electrolytes. The ionic conductivities of composite gel electrolytes are slightly lower than the counterpart liquid electrolyte at all the evaluated temperatures; the filler types (silica oxide and oxide mixture) and the surface groups (hydrophilic and hydrophobic) do not have a significant effect on conductivity at the experimental conditions employed. We have conducted the measurements for the interfacial stability both at room temperature (~ 23°C) and low temperature (3 ~ 5°C). Li/electrolytes/Li cells were cycled at current density of 0.2 mA/cm² with fixed charged density 36 mC/cm². Four different electrolytes based on 1M LiPF₆ + EC: EMC were used to evaluate the interfacial stability: (1) liquid; (2) 10 wt% A200 gel; (3) 10 wt% R805 gel; (4) and 10wt% COX84 gel. The preliminary results show that the average half-cell voltage increases for the liquid electrolyte; while the average half-cell voltage was more stable with fumed oxides. Adding fumed oxides improves the interfacial stability of lithium/electrolyte at both low and room temperatures.

We have studied the lithium interfacial stability of single-ion conducting fumed silica-based mixed-molecular weight (MW) polymer electrolytes: Degussa R711-poly(lithium 2-acrylamido-2-methyl-1-propanesulfonate) (R711-pLiAMPS, surface Li⁺ concentration $\gamma = 4.2 \text{ nm}^{-2}$) + PEO (MW = 600K) + PEGdm (MW = 250) (PEO:PEGdm mass ratio = 1:1). Lithium imide salt (LiTFSI) was added to some mixtures to provide additional charge carriers, and a constant Li(LiTFSI + LiAMPS):O mole ratio of 1:60 was used in experiments. The interfacial stability was studied under a lithium deposition–dissolution cycling condition, i.e., applying a current of 0.05 mA cm⁻² on Li/electrolyte/Li cells, and the current was reversed every 1 h (180 mC cm⁻²). The average cell voltage of Li/R711-pLiAMPS + mixed-MW PEO electrolyte/Li is lower than that of Li/R711-pLiAMPS + high-MW PEO electrolyte/Li due to the higher room-temperature conductivity of R711-pLiAMPS + mixed-MW PEO electrolyte arising from the disturbed PEO crystallization in mixed-MW PEO. The average voltage of Li/LiTFSI + mixed-MW PEO/Li cell increases dramatically after 100 cycles, however, Li/R711-pLiAMPS + LiTFSI + mixed-MW PEO electrolyte/Li cells show no appreciable voltage increase after 300 cycles, indicating R711-pLiAMPS has the ability to improve lithium interfacial stability.

- **Further plans to meet or exceed milestones:** We will continue collaboration with BATT investigators Drs. DesMarteau and Creager to test their new imide salts.
- **Reason for changes from original milestone:** N/A

TASK STATUS REPORT

PIs, INSTITUTION: D. DesMarteau and S. Creager, Clemson University

TASK TITLE – PROJECT: Electrolytes - New Battery Electrolytes Based on Lithium Fluorosulfonate and Fluorosulfonimide Salts

SYSTEMS: Graphite / $\text{LiPF}_6 + \text{EC}:\text{DEC}$ / LiFePO_4

BARRIERS: Poor electrolyte transport, low power, short life, abuse tolerance.

OBJECTIVES: (1) Synthesize new lithium fluorosulfonate and fluorosulfonimide salts for which anion attachment to a suitable plasticizer, scaffold or matrix can be accomplished; (2) Characterize battery electrolytes made from the target salts with respect to structure, transport properties (conductivity, salt diffusion, transference), reactivity (e.g. with electrode materials and current collectors), and battery performance (power, fade, interface stability).

APPROACH: Salts will be synthesized using variants of methods developed at Clemson over the last 15 years (D. DesMarteau, J. Fluorine Chem. 1995, 72, 203-208). Transport properties will be measured using EIS combined with restricted diffusion and potentiostatic and galvanostatic polarization techniques as needed. Reactivity with electrode materials will be studied by calorimetry, and half-cell and full-cell cycle testing will be performed using standard techniques with assistance from and/or in collaboration with other BATT researchers.

STATUS Oct. 1, 2004: Oligomeric salts of structure $\text{CF}_3\text{SO}_2[\text{N}(\text{Li})\text{-SO}_2\text{R}_f\text{SO}_2]_n\text{N}(\text{Li})\text{SO}_2\text{CF}_3$ were provided to BATT coworkers for half-cell, rheology, and Al corrosion testing. Allyl ether salts of structure $\text{CH}_2=\text{CHCH}_2\text{O-CF}_2\text{CFH-OCF}_2\text{CF}_2\text{-salt}$ where salt = $\text{SO}_3(\text{Li})$ and $\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3$ were provided to BATT coworker Kerr for use making single-ion conductors. Transport studies on SPEs prepared using oligomeric fluorosulfonimide salts will be completed. Ionic melts of structure $\text{PEG-O-CF}_2\text{CHFO-CF}_2\text{CF}_2\text{-salt}$ will have been synthesized and preliminary characterization including conductivity studies completed.

EXPECTED STATUS SEPT. 30, 2005: Plasticized electrolytes of general structure $(\text{X})\text{-O-CF}_2\text{CHFO-CF}_2\text{CF}_2\text{-salt}$ where salt = SO_3Li or $\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3$ and X = PEG, polyether, polysiloxane, and silica will have been synthesized and characterized with respect to conductivity and reactivity, and samples provided to other BATT workers for further testing.

RELEVANT FREEDOMCAR GOALS: 15 year life, <23% power fade, specific power 625 W/kg at the system level.

MILESTONES:

- (1) Synthesize new electrolytes of general structure $\text{X-O-CF}_2\text{CHFO-CF}_2\text{CF}_2\text{-salt}$ where salt = SO_3Li or $\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3$ and X = a PEG oligomer, a comb-branch network polyether, an OH-functionalized siloxane polymer, or a functionalized fumed silica particle. May 05.
- (2) Characterize the resulting electrolytes with respect to structure, transport properties, reactivity with anode and cathode materials, and battery performance using EIS, scanning calorimetry, half-cell and full-cell cycle testing, and other techniques as needed. Sept 05.

PROGRESS TOWARD MILESTONES:

Synthesis of pure ionic melts of structure $X\text{-OCF}_2\text{CFH-OCF}_2\text{CF}_2\text{-salt}$ where X = PEG oligomer of MW 550 (average of 11.8 ethylene oxide units per chain) and salt = SO_3Li or $\text{SO}_2\text{N(Li)SO}_2\text{CF}_3$ has been achieved. Problems with impurities and side reactions noted in prior reports were eliminated by a combination of working at lower temperatures, using less solvent, and mixing reactants gradually instead of all at once. ^1H and ^{19}F NMR spectra revealed no unassigned peaks, and the salt-to-oxygen ratio obtained from ^1H NMR spectral integration is within experimental error of that expected for a pure material, confirming that samples are devoid of any unreacted polyether.

Figure 1 presents ionic conductivity data for two ionic melts, one with a fluorosulfonate anion and the other with a fluorosulfonimide anion linked to a PEG chain. Both samples show high conductivity at all temperatures, with the sulfonimide sample showing consistently higher conductivity by factors of between 1.5 and 1.7 relative to the sulfonate at a given temperature. Experiments planned for the near future will seek to evaluate melt viscosity, salt concentration polarization (as revealed by impedance changes during potentiostatic polarization), reactivity with electrode materials, and cycling behavior in half-cell and full-cell configurations. To enable these studies, synthetic procedures are being reconsidered with the aim of scaling up production to multi-gram levels.

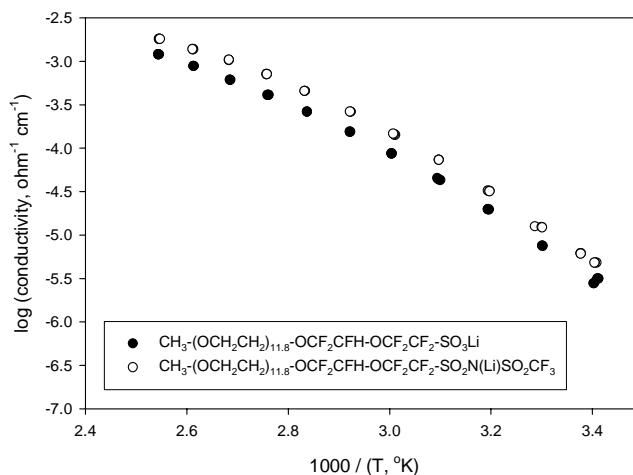


Figure 1. Ionic conductivity of a pair of polyether-based lithium fluorosulfonate and fluorosulfonimide ionic melts.

Preliminary results on alternate and potentially easier and less expensive approaches to synthesizing polyether-based lithium-conducting ionic melts have also been obtained. In one approach, deprotonated PEG oligomers react with salt-functionalized aryl iodides of general structure $\text{I-C}_6\text{H}_4\text{-Salt}$ to displace iodide. In another approach, deprotonated PEG oligomers react with diazonium-functionalized zwitterions of general structure $\text{N}_2^+\text{-C}_6\text{H}_4\text{-anion}$. The latter reaction is especially attractive because the only side product is nitrogen gas which is easily removed. In both cases, the result is attachment of a PEG chain onto a phenyl ring which is also substituted with the lithium salt of a suitable anion. Preliminary NMR spectral data indicate that all of the proposed reactions are working as expected. Work planned for the near future will focus on obtaining sufficient amounts of material in pure form to enable electrochemical testing.

Finally, we recently succeeded in making a lithium fluorosulfonimide epoxide salt of structure $\text{CH}_2\text{OCHCH}_2\text{-OCF}_2\text{CFH-OCF}_2\text{CF}_2\text{-SO}_2\text{N(Li)SO}_2\text{CF}_3$. Synthesis was achieved in high yield with minimal side products. Work in progress is exploring the polymerization and other reaction chemistry of this novel lithium fluoroanion salt.

TASK STATUS REPORT

PI, INSTITUTION: G.D. Smith and O. Borodin, University of Utah

TASK TITLE - PROJECT: Electrolytes - Molecular Modeling of Solid Polymer Electrolytes, Single Ion Conductors and Gel Electrolytes

SYSTEMS: Low -cost Li-ion

BARRIERS: Poor cation transport properties of gel electrolytes at ambient temperatures. Poor transport through SEI layer and poor chemical stability of the SEI layer.

OBJECTIVES: Gain molecular level understanding of the cation transport mechanism in single ion conductor gel electrolytes. Develop new single ion conductor gel electrolytes with improved ion transport and mechanical properties. Understand Li transport in the SEI layer at the SEI layer/electrolyte interface.

APPROACH: Perform virtual synthesis and detailed characterization of a number of single ion conductor electrolytes. Vary the structure of the single ion conductor and the fraction of the plasticizer (ethylene carbonate, or EC) in gel electrolytes in order to optimize the ion transport and mechanical properties of polymer electrolytes. Perform MD simulations of the SEI layer and SEI/electrolyte interface to predict structural properties and Li transport of these battery components.

STATUS OCT. 1, 2004: Molecular dynamics (MD) simulations have been performed on a number of single ion conductors based on polyether type comb-branched polymers with TFSI anions attached to side chains and ionic liquids with the structure $\text{LiTFSI-EO}_n\text{-TFSILi}$ as a function of temperature. The length of side chains, the Li^+ cation concentration and the concentration of EC will be varied in order to determine the structure with the best ion transport parameters. Temperature dependence of the transport properties of gel electrolytes will be investigated at one concentration of plasticizer.

EXPECTED STATUS SEPT. 30, 2005: A detailed study of the influence of comb-branched copolymer architecture and plasticizer concentration on structural and transport properties of single ion conductor gel electrolytes as a function of temperature will be investigated for the following parameters: the length of side chains and their spacing, salt concentration, and amount of plasticizer. The structure of the alkyl carbonate component of the anode SEI layer will be predicted. Lithium transport in the SEI layer components and at the interface of the SEI with the gel electrolyte will be studied on the molecular level using MD simulations.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade

MILESTONES: 1) Complete investigation of the effect of the length of side chains, salt concentration and EC concentration on structural and transport properties of single-ion conductor gel electrolytes at three temperatures. (June 1, 2005)
2) Finish investigation of the anode SEI layer structure, lithium transport, and interface with the gel electrolytes. (Sept. 2005)

PROGRESS TOWARD MILESTONES

Molecular dynamics simulations have been performed on a number of ionic liquids with the structure $\text{LiTFSI}-(\text{EO})_n\text{-LiTFSI}$ $n=12, 20, 40$; gel and dry single ion conductors of various architectures with the (trifluoromethanesulfonyl) imide anion immobilized on the comb-branched polymer-host side chains as shown in Fig. 1. At 423 K a maximum conductivity was observed for single ion conductors with the structure corresponding to the $\text{EO}:\text{Li}=20:1$ and $\text{EO}:\text{Li}=40:1$ salt concentration. Temperature dependence on the lithium transport was investigated for $\text{PEPE}_{10}\text{TFSI-Li}$ single ion conductor (see Fig. 1 for notation), $\text{PEPE}_5\text{TFSI-Li} + \text{EC}_6$ gel single ion conductor $\text{PEPE}_5\text{TFSI-Li} + \text{EC}_6$ and $\text{LiTFSI}-(\text{EO})_n\text{-LiTFSI}$ ionic liquid and is shown in Fig. 1. Gel single ion conductor exhibited the smallest activation energy and the largest conductivity at low temperatures. Extrapolation of the gel electrolyte conductivity to room temperature yields a rather high value of 0.1 mS/cm for a relatively low weight fraction of plasticizer 37 wt%. Extrapolation of the dry single ion conductor and ionic liquid conductivity to low temperatures yields room temperature conductivity around 0.02 mS/cm.

In order to provide molecular level understanding and characterization of the structural and transport properties of the reversibly and irreversibly adsorbed electrolyte on the electrode surfaces during battery operation, we initiated non-equilibrium MD simulation studies of the electrolyte (EC/LiTFSI) in contact with the blocking for anion but nonblocking for Li^+ model electrode surface. Electrolyte was subjected to the electric field resulting in development of concentration profiles. After steady state is reached, we will perform analysis of the structure and dynamics in the Helmholtz plane and diffuse double layer developed next to the model electrode surface.

In parallel to the above simulations, we performed quantum chemistry calculations and developed many-body polarizable force field for dilithium alkyl carbonate – a commonly observed component of the outer SEI layer. Molecular dynamics simulations of dilithium alkyl carbonate are underway at 393 K.

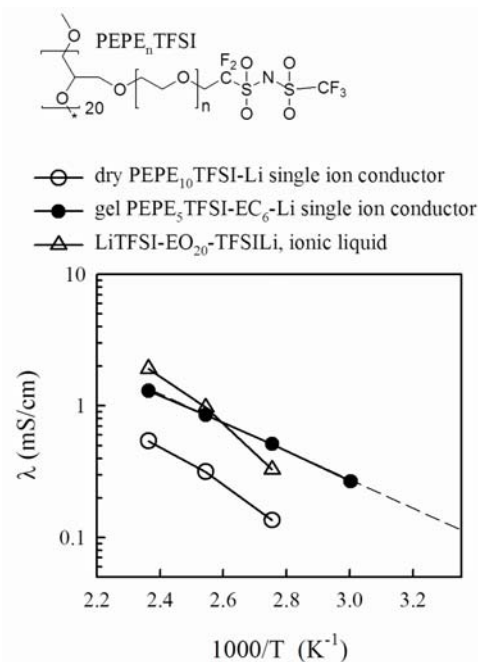


Figure 1. Conductivity of the ionic liquid, dry and gel single ion conductors from MD simulations. The $\text{PEPE}_5\text{TFSI-EC}_6\text{-Li}$ gel single ion conductor was simulated at the (ether oxygen + ethylene carbonate)/ $\text{Li}=11$ salt concentration.

BATT TASK 4 CATHODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes - Novel Materials

SYSTEMS: High-voltage, high energy: Gr/LiPF₆+EC:DEC/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂
High-voltage, high power: Gr/LiBOB+gBL:EA/LiMn₂O₄

BARRIER: Cost and abuse tolerance of Li-ion batteries

OBJECTIVE: To develop low cost, high-energy and high-power Mn-oxide-based cathodes.

APPROACH: Our approach is to search for, characterize, and develop low-cost manganese oxide cathodes for Li-ion cells. We will continue to focus our work on high-voltage, high-capacity layered lithium-manganese oxide ‘composite’ $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ structures with particular emphasis on electrodes in which $\text{M}' = \text{Mn}$ and $\text{M} = \text{Mn, Ni, Co}$ that operate between 3.0 and 4.8 V vs. Li^0 . These materials are showing excellent promise to replace LiCoO_2 as the cathode of choice for lithium-ion batteries; they also hold promise for high-power applications. We will also attempt to exploit high-potential LiM_2O_4 spinel materials (4.0-5.0 V vs. Li^0) for high-power batteries. In conjunction with our anode project (Task 2.1), we will explore the electrochemical properties and the abuse tolerance of high-potential layered and spinel cathodes against graphite and low-potential metal oxide anodes.

STATUS OCT. 1, 2004: It was demonstrated that a rechargeable capacity of 170-180 mAh/g could be delivered by $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ composite electrodes in lithium cells for 100 cycles between 4.5 and 3.0 V at 50 °C. It was discovered that the irreversible capacity loss on the initial cycle could be reduced by pre-conditioning the electrodes with acid. A capacity in excess of 110 mAh/g was achieved from spinel electrodes when cycled between 5.0 and 3.5 V vs. lithium which augers well for the development of stable high-voltage (>4.5 V) Li-ion cells. Evaluation of high-potential layered and spinel cathodes against metal oxide anodes had been initiated.

EXPECTED STATUS SEPT. 30, 2005: Improvements in the electrochemical performance of $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ electrodes will have been achieved. High capacity $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ layered electrodes and high rate LiM_2O_4 (4.0 – 5.0 V) spinel electrodes with a high Mn content will have been evaluated against graphite and metal oxide negative electrodes.

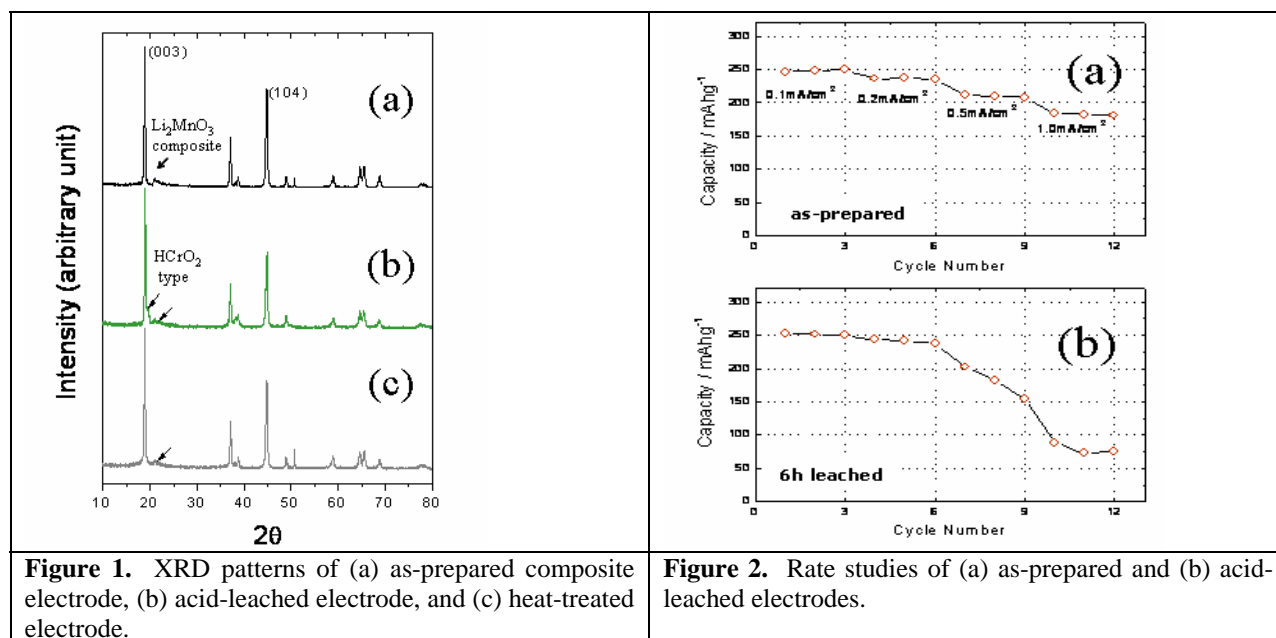
RELEVANT USABC GOALS: 300,000 shallow discharge cycles (HEV requirement); 10 year life, <20% fade over a 10-year period.

MILESTONES (by 30 September 2005): 1) Evaluate $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ composite electrodes with a high Mn content against a technical target of 200 mAh/g for 100 cycles between 4.8 and 3.0 V vs. Li^0 at room temperature and at 50 °C; 2) Evaluate the rate capability and low-temperature behavior of layered $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ and spinel LiM_2O_4 electrodes; and 3) evaluate the layered and spinel cathodes against graphite and metal oxide anodes.

PROGRESS TOWARD MILESTONES

In previous quarterly reports we have described our strategy to use layered-layered composite oxides, denoted $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ (in which M' and M are Mn and Mn/Ni, respectively), to design high capacity (>250 mAh/g) cathodes. We have examined the reactivity of these materials at high potential (~ 4.6 V) and have observed a large first cycle irreversibility loss ($>25\%$). Subsequent investigations showed that acid-leaching can be effective in reducing and even eliminating this first cycle irreversible loss, while preserving a high discharge capacity. We have continued these studies to evaluate the acid-leaching process and the reaction mechanism in composite electrodes of nominal composition $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{Li}[\text{Ni}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}]\text{O}_2$. Figure 1 shows X-ray diffraction patterns of (a) the as-prepared electrode, (b) a 6-h acid-leached sample, and (c) sample (b) after a heat-treatment step. The shoulder on the (003) peak (at slightly higher 2θ) in Fig. 1b is indicative of a layered HCrO_2 -type phase, similar to that formed by acid-leaching Li_2MnO_3 ¹, thereby providing supportive evidence for the ‘composite’ (two-component) character of the electrode and for a localized acid-leaching process whereby Li_2O is removed preferentially from Li_2MnO_3 domains of the $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{Li}[\text{Ni}_{0.375}\text{Co}_{0.25}\text{Mn}_{0.375}]\text{O}_2$ structure. On heat-treatment, this metastable HCrO_2 -type phase transforms into the configuration of the parent composite structure (Fig. 1c).

The rate capability of as-prepared and acid-treated electrodes has also been evaluated (Fig. 2a and Fig. 2b, respectively). Acid-leached electrodes do not perform as well as untreated electrodes at high current rates. Further work is planned to address and overcome this issue.



We are extending the concept of layered-layered composite electrodes to layered-spinel electrodes, such as $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiM}_2\text{O}_4$, in which $\text{M}=\text{Li}, \text{Mn}, \text{Co}, \text{Ni}$ with a focus on electrodes with a high-Mn content. Our strategy is to design a bi-functional electrode structure in which the layered component ensures a high capacity while the spinel component ensures a high-rate capability. Our initial data indicate that capacities >250 mAh/g are achievable.

Reference:

¹Y. Paik, C. P. Grey, C. S. Johnson, J.-S. Kim, and M. M. Thackeray, *Chem. Mat.*, **14**, 5109-5115 (2002).

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Cathodes – Novel Materials

SYSTEMS: Li-Ion high-voltage, high energy and low voltage-high stability

BARRIER: Lower-cost, higher power, higher-capacity and abuse-tolerant safer cathodes

OBJECTIVES: The primary objectives are to find (a) lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, and (b) high-rate HEV compatible cathodes, both of which are based on environmentally benign materials.

APPROACH: Our cathode approach is to place emphasis on manganese dioxides, both pure and modified with other transition metals, using predominantly low temperature synthesis approaches. These materials will be synthesized, and characterized both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT. 1, 2004: We have determined that layered manganese dioxides can be structurally stabilized, and that their electronic conductivity and cycling can be significantly enhanced by the addition of other transition metals. Addition of other transition metals also prevents structure change at low lithium content to one-block or spinel structures, and changes oxygen evolution behavior. We have completed an evaluation of LiFePO_4 as a base-case low cost cathode, and shown that it is intolerant of deep over-discharge. We also have shown that vanadium oxides can also be stabilized by the addition of ammonium and manganese ions to attain capacities over 200Ah/kg.

- LiFePO_4 : > 120 Ah/kg for 100 cycles at 1 mA/cm².
- Layered $\text{Li}_x\text{Co}_z\text{Ni}_y\text{Mn}_{1-y-z}\text{O}_2$: 175 Ah/kg and 150 Ah/kg for 30 cycles at 1 and 2 mA/cm² respectively.
- Layered $\text{A}_z\text{Mn}_{0.1}\text{V}_2\text{O}_5$ (A= NH_4 or TMA): \geq 200 Ah/kg for 6 cycles.

EXPECTED STATUS SEPT. 30, 2005: For low-cost Li-Ion cells, we expect to identify the changes in (a) electrochemistry, (b) oxygen evolution (abuse tolerance), (c) high rate capability (HEV), (d) coating effectiveness and (e) the electronic conductivity of LiMnO_2 structures as a function of substitution level as in $\text{Li}_x\text{Mn}_{1-y-z}\text{Ni}_y\text{Co}_z\text{O}_2$, so as to determine the optimum minimum substitution level. We will also have evaluated possible variants on iron phosphate as base case cathodes, and explored some higher capacity next generation cathodes.

RELEVANT USABC GOALS: 300,000 shallow discharge cycles, and abuse tolerance to cell overcharge and short circuit

MILESTONES: Our major milestones this year are: (a) to characterize the electronically stabilized manganese oxide, determine the optimum substitution of Mn to obtain a stable high rate abuse tolerant cathode (including application to HEV), and to compare the best samples with iron phosphates by July 2005, and (b) to search for, identify and characterize some new low cost higher energy density cathode materials and to compare the best samples with the base-line chemistries (continuing).

PROGRESS TOWARD MILESTONES

Iron Phosphates. This Quarter we continued our studies of lithium iron phosphate and related structures. An evaluation of the available conductivity and diffusion data on LiFePO_4 shows that the ionic conductivity of this material is less than 10^{-9} S/cm, which results in a Li diffusion coefficient of no more than 10^{-13} to 10^{-14} cm^2/sec . We have identified $\text{LiMn}_{1-y}\text{Fe}_y\text{PO}_4$ as a suitable model compound to measure the true diffusion coefficient as a single-phase region is reported to exist around the composition $\text{Li}_y\text{Mn}_{1-y}\text{Fe}_y\text{PO}_4$; moreover this system shows a high Li vacancy concentration, which should allow more ready lithium migration.

If the iron to phosphate ratio can be increased from that in LiFePO_4 , then it should be possible to increase the inherent cathode capacity beyond 170 mAh/g. We have successfully synthesized the all ferric $\text{Fe}_{1.36}\text{PO}_4(\text{OH})$ compound, in which one third of the available iron sites are vacant (the all ferrous compound $\text{Fe}_2\text{PO}_4(\text{OH})$ has all the iron sites occupied). The cycling behavior of this compound is shown in Fig. 1(a) below, where the capacity obtained at 21°C is 170 mAh/g, approaching the theoretical value of 192 mAh/g. The protons in this compound can be partially exchanged for lithium ions. This ion-exchanged material shows improved capacity retention on cycling, as shown for a sample ion-exchanged by heating with lithium nitrate in Fig. 1(b). The fully discharged compound has around 2 Li/ PO_4 group. We are presently trying to identify the locations of the lithium and hydrogen ions in these compounds, working with C. Grey.

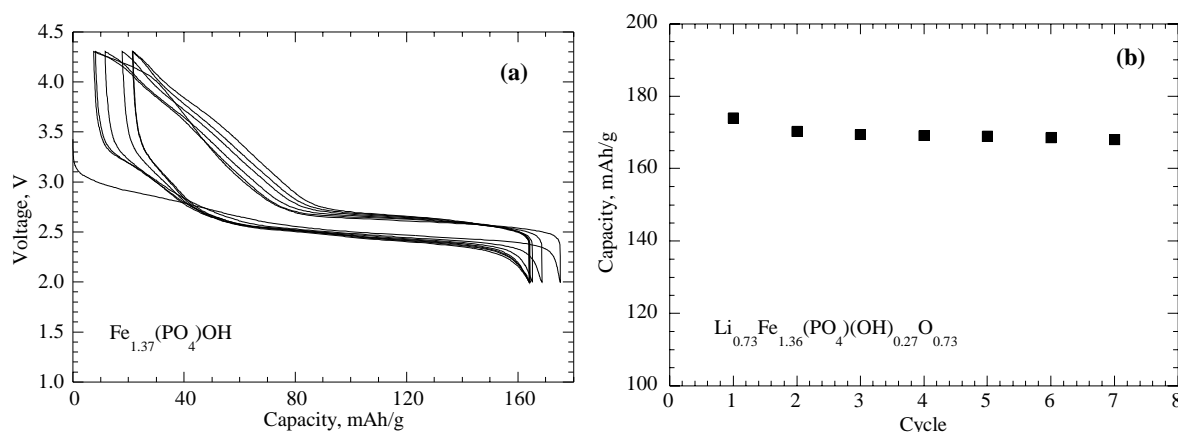


Figure 1. (a) Cycling of Li^+ in $\text{Fe}_{1.37}(\text{PO}_4)\text{OH}$, at $0.5 \text{ mA}/\text{cm}^2$ (15 mA/g) and (b) the capacity on cycling of $\text{Li}_{0.73}\text{Fe}_{1.36}(\text{PO}_4)(\text{OH})_{0.27}\text{O}_{0.73}$ at $0.2 \text{ mA}/\text{cm}^2$ (15 mA/g). The complete reduction of all the ferric to ferrous would result in a capacity of 192 mAh/g.

Further plans to meet or exceed milestones: None

Reason for changes from original milestones: No changes

Publications and Presentations resulting from the work.

1. M. S. Whittingham, "Lithium Batteries and Cathode Materials", Chemical Reviews, 2004, **104**, 4271-4301.
2. M. S. Whittingham, "Advanced Batteries", October 28, 2004, General Electric, Global Research, Niskayuna, NY.
3. Miaomiao Ma, Natasha Chernova, Peter Y. Zavalij and M. Stanley Whittingham, "Structural and Electrochemical Properties of $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ ", MRS Meeting, Boston, MA December 2nd 2004.
4. Soft Chemistry Approaches to New Materials for Electrochemical Energy Storage", November 5th. 2004, Chemistry Department, North Carolina State University, NC.

TASK STATUS REPORT

PI, INSTITUTION: M. Doeff, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cathodes - Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium-Ion Batteries

SYSTEMS: Low-voltage, high-stability (LiFePO_4), high-voltage, high energy ($\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, new manganese oxides), and high voltage, high-power (new manganese oxides)

BARRIERS: Cost, cycle life, safety, energy density, and power density

OBJECTIVES: To develop low-cost cathodes based on benign materials (manganese oxides, lithium iron phosphates, etc.) having electrochemical characteristics (e.g., cycle life, energy and power densities) consistent with the goals of the USABC and/or FreedomCar.

APPROACH: Cathode materials are synthesized by various means. Physical and electrochemical properties (e.g., structure, surface characteristics) are measured in conjunction with members of the diagnostic tasks. Emphasis is placed on low-cost, structurally stable materials such as manganese oxides and lithium iron phosphate, as well as novel materials with the potential for high energy density.

STATUS OCT. 1, 2004: Electrochemical characterization of $\text{Li}_x\text{Al}_y\text{Mn}_{1-y}\text{O}_{2+z}$ O2/O3 intergrowths was completed. Experiments determining the optimum amount of pyromellitic acid (PA) for carbon-coating LiFePO_4 were completed, and those using Fe promoters of graphene formation are underway.

EXPECTED STATUS SEPT. 30, 2005: Initial screening of novel manganese oxides for abuse-tolerance will be complete, and materials will be recommended for high-power applications based on results. *In situ* carbon structure, electrochemical performance, and synthetic parameters (e.g., promoter to PA ratios) used in making coated LiFePO_4 will be correlated. New manganese oxide structures without Ni or Co substituents for high-energy density applications will continue to be surveyed.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES:

- a) Determine best synthetic conditions (promoter to PA ratios, etc.) for carbon-coating LiFePO_4 . (June 2005)
- b) Recommend the most abuse-tolerant manganese oxide structures for potential HEV applications, and highest energy density manganese oxides containing no Ni or Co for potential high energy applications. (Sept. 2005)

PROGRESS TOWARD MILESTONE (a)

LiFePO₄ samples calcined with either 6 or 8 wt% pyromellitic acid (PA) and 1% ferrocene were electrochemically characterized. (These materials contain 1.45 and 1.64% residual carbon respectively). Figure 1 shows a comparison of rate data for cells containing LiFePO₄ prepared with and without PA and iron nitrate or ferrocene promoters.

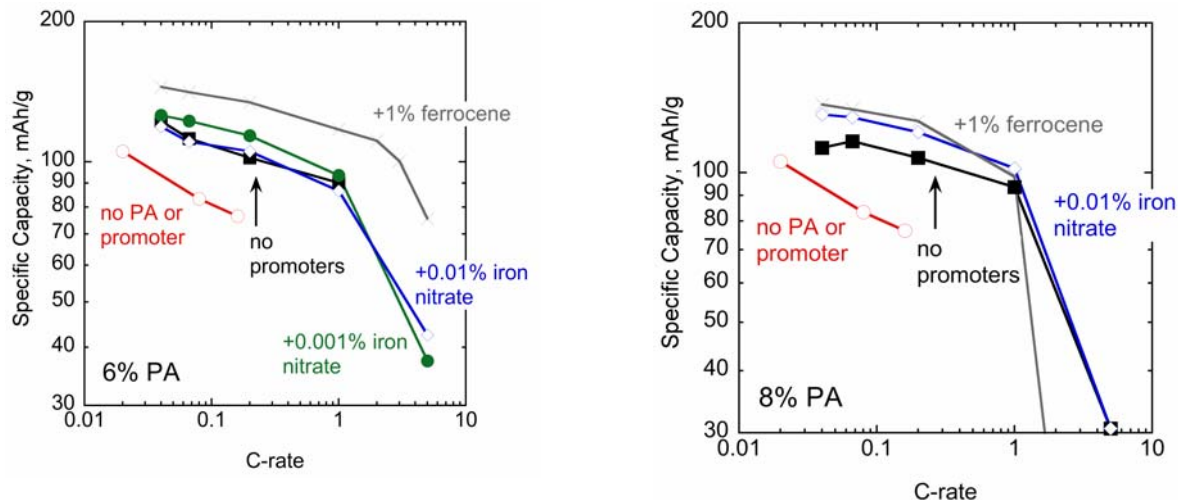


Figure 1. Rate data for Li/LiFePO₄ cells containing cathode materials prepared with 6% PA (left) or 8% PA (right) and iron nitrate or ferrocene promoters. Results on samples prepared without promoters and PA are included for comparison.

The addition of ferrocene during synthesis results in markedly better performance for the 6% PA series, but not the 8% series. The *in situ* carbon structure studied by Raman microprobe spectroscopy (Kostecki, Task 5.1) indicates lowered sp³ carbon content and D/G ratios, resulting in higher electronic conductivity for the better performing material. Mixing difficulties and the volatility of ferrocene cause irreproducibility during sample synthesis. For this reason, we intend to replace it with ferrocenecarboxylic acid, which is expected to have a different decomposition route and will be less volatile. We will also characterize cells built with carbon-coated current collectors to determine how much the resistance at the current collector/cathode interface affects rate capability.

Cu₂Mn₃O₈ and Ca₂Mn₃O₈ were synthesized by hydrothermal and sol-gel processes, respectively, and are currently being characterized electrochemically.

Further plans to meet or exceed milestones N/A

Reason for changes from original milestones N/A

Publications and Presentations:

“Investigation of Layered Intergrowth Li_xM_yMn_{1-y}O_{2+z} (M=Ni, Co, Al) Compounds as Positive Electrodes for Li-ion Batteries”, M. Dollé, J. Hollingsworth, T. J. Richardson, and M. M. Doeff, **Solid State Ionics**, 175/1-4, 225 (2004).

“Electrochemical Performance of Aluminum-substituted Layered Manganese Oxide Intergrowth Structures”, Marca M. Doeff, Joel Hollingsworth, and Mickael Dollé, **Electrochem. Soc. Meeting**, Orlando, FL 2003 Vol. 2003-2, abstract 334.

TASK STATUS REPORT

PI, INSTITUTION: J.B. Goodenough, University of Texas at Austin

TASK TITLE - PROJECT: Cathodes - Novel Materials

SYSTEMS: Li secondary battery

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To evaluate alternative *cathode* materials for a lithium-ion battery.

APPROACH: The universal motif of cathodes in rocking chair Li^+ -ion batteries is one of immobilized redox centers that are accessible to electrons from the current collector and Li^+ ions from the electrolyte. Immobilization ensures that the redox units do not transfer to and subsequently poison the anode. Our research is centered around high-power cathodes for the purpose of EV and HEV's. This translates into pure or composite materials which allow for transfer of electrons *and* Li^+ ion with little or no resistance. We are currently pursuing three different avenues of research: (1) New materials based on conventional oxide structures with proven high rate capabilities, (2) new cathode schemes based on conductive polymers which may serve either as self-contained cathodes or as a new conductive binder in more conventional composite cathodes, and (3) Substitution into the environmentally benign and cost effective LiFePO_4 to improve rate capabilities.

STATUS OCT. 1, 2004: Well-ordered $\text{LiNi}_{1-x}\text{Mn}_x\text{O}_2$ has been prepared and battery testing has shown good cyclability. A principle for predicting cation order/disorder in layered materials with an $\alpha\text{-NaFeO}_2$ structure has been developed. Preliminary rate tests are in progress.

EXPECTED STATUS SEPT. 30, 2005:

- Electrochemical testing of our high-rate layered material to elucidate the limiting parameter will have been completed.
- Preliminary analysis of substitution into the Fe site of LiFePO_4 will have been completed.
- The feasibility of polypyrrole as a conducting binder/scaffolding will have been explored.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES:

1. Electrochemical testing of our high-rate layered material to elucidate the limiting parameter. (Feb. 2005)
2. Preliminary analysis of substitution into the Fe site of LiFePO_4 . (Aug. 2005)

PROGRESS TOWARD MILESTONES

(a) $\text{LiNi}_{1-x}\text{Mn}_x\text{O}_2$ ($x < 0.5$). Among the oxides, the layered LiMO_2 structure offers the best hope for high current capabilities provided complete ordering of the Li and M atoms can be achieved. Complete order requires a significant difference in the ionic radius of the Li^+ ion and the mean ionic radius of the M atoms. We use a low-temperature preparation route for LiMO_2 with $\text{M} = \text{Ni}_{1-x}\text{Mn}_x$, $x < 0.5$, to achieve a high degree of order of the Li atoms into alternate cation layers. Co-precipitation of $(1+\delta)\text{Li}$ with $(1-x)\text{Ni}$ and $x\text{Mn}$ acetate aqueous solution was achieved with oxalic acid. Samples fired at 900°C in air for 5 hrs gave the X-ray diffraction patterns of Fig.1. Fig.2 shows the discharge curves between 4.3 and 3.0 V for $x = 1/3$ and current densities from 0.1 to 8 mA/cm^2 . Fig.3 compares the reversible capacity fade with increasing current density, and Fig.4 compares the rate capability for $x = 1/3$ and 0.46 with that of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. The X-ray data confirm excellent Li^+ -ion ordering for $x = 1/3$, and the rate capability of the $x = 1/3$ sample is shown to be comparable to that of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, but without the presence of any Co. A small capacity fade with repeated cycling differed from our earlier experience with ball-milled materials. We will test the capacity fade of $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ cathodes that have been ball-milled.

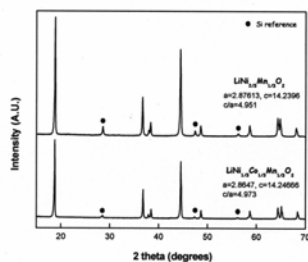
(b) $\text{Li}[\text{Cr}_2]\text{O}_4$. Although the Li^+ -ion mobility is not expected to be high in an oxospinel, preparation and evaluation of the spinel $\text{Li}[\text{Cr}_2]\text{O}_4$ represents investigation of a new material, and the consortium had indicated interest in spinels. We have shown that we can displace copper from $\text{Cu}[\text{Cr}_2]\text{O}_4$ with n-butyl lithium, and we will be characterizing our product chemically and electrochemically next quarter. This study was not one of our original milestones.

(c) *FAPP polymer*. We have now succeeded in preparing ferrocene groups attached to a polypyrrole backbone immersed in a LiPF_6 electrolyte. Electrochemical testing of these initial preparations has been initiated.

$\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$ system

Synthesis:

Co-precipitation of $(1+\delta)\text{Li}:(1-x)\text{Ni}:x\text{Mn}$ acetate aqueous solution by using oxalic acid & Firing at 900°C for 5 hours in air



Rate capability:

Constant charge current density (0.1 mA/cm^2)
& varying discharge current density from 0.1 to 8 mA/cm^2
Voltage window is from 3 to 4.3 V vs Li/Li^+

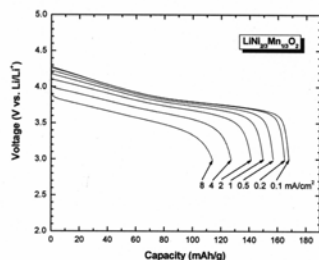


Figure 1 and 3

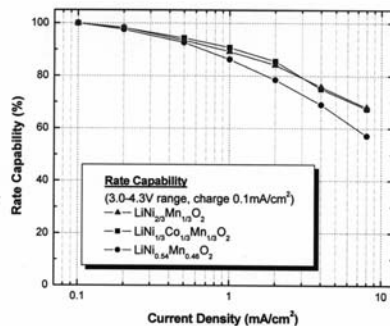
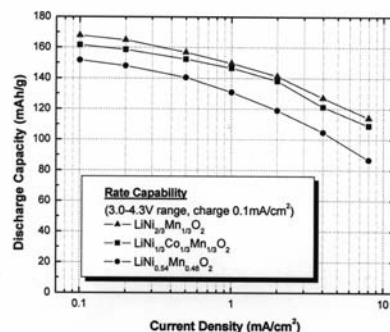


Figure 2 and 4

TASK STATUS REPORT

PI, INSTITUTION: A. Manthiram, University of Texas at Austin

TASK TITLE - PROJECT: Cathodes - Superior Capacity Retention, High Rate Spinel Manganese Oxide Compositions

SYSTEMS: Spinel manganese oxides

BARRIERS: Cycle life, elevated temperature storage, power density, and energy density

OBJECTIVES: To develop low-cost spinel manganese oxide compositions that can offer excellent capacity retention, high rate, low irreversible capacity loss, and good storage characteristics at elevated temperatures.

APPROACH: Our approach is to develop a firm scientific understanding of the factors that control/influence the electrochemical performance of the spinel oxide cathodes and utilize the knowledge gained to design and develop high performance spinel manganese oxide compositions. In this regard, a variety of single and multiple cationic substitutions as well as an optimization of the microstructure and morphology are being pursued.

STATUS OCT. 1, 2004: A variety of multiple cationic substitutions in the spinel LiMn_2O_4 system and an evaluation of the electrochemical performances of the various compositions have established a clear correlation of the electrochemical properties to some basic materials parameters such as the initial manganese valence and the lattice parameter difference Δa between the two cubic phases formed during the charge-charge process.

EXPECTED STATUS SEPT. 30, 2005: Evaluation of the optimized $\text{LiMn}_{2-y-z}\text{Ni}_y\text{Li}_z\text{O}_4$ and $\text{LiMn}_{2-y-z-\eta}\text{M}_y\text{Li}_z\text{M}'_{\eta}\text{O}_4$ (M and M' = transition and non-transition metal ions) spinel oxide compositions (4 V) in lithium ion cells, identification of the factors that control the electrochemical performances of the cation-substituted 5 V spinel oxide system $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, and a comparison of the factors with those of the 4 V spinel oxide cathodes.

RELEVANT USABC GOALS: 10-year life, < 20 % capacity fade over a 10-year period

MILESTONES:

1. Evaluation of the optimized 4 V spinel oxide cathodes in lithium ion cells. (Mar. 2005)
2. Identification of the factors controlling the electrochemical performances of the cation-substituted 5 V spinel oxide system $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$. (Sept. 2005)

PROGRESS TOWARD MILESTONES

In continuation of our multiple cationic substitutions in the spinel LiMn_2O_4 system and recognizing that a cosubstitution of both Li and Ni/Cu for Mn improves the electrochemical performance significantly in the 4 V region, we have pursued additional spinel compositions such as $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Al}_{0.075}\text{O}_4$, $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Ni}_{0.04}\text{Al}_{0.035}\text{O}_4$, and $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Cu}_{0.04}\text{Al}_{0.035}\text{O}_4$. Among them, the $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Ni}_{0.04}\text{Al}_{0.035}\text{O}_4$ composition is found to show slightly higher capacity values (~ 100 mAh/g) and better elevated temperature cyclability than our previous best compositions such as $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Ni}_{0.075}\text{O}_4$. We are in the process of comparing the rate capability and storage performance of these new compositions with those of our previous best compositions as well as correlating the electrochemical performance to the lattice parameter difference between the two cubic phases formed during the charge-discharge process. Additionally, we have begun to examine the different spinel compositions before and after cycling as well as at various depths of charge by micro-Raman spectroscopy in collaboration with the University of Puerto Rico at San Juan to enhance further our understanding of the factors controlling the electrochemical performance of spinel oxide cathodes. Preliminary data suggest that while the LiMn_2O_4 cathode develops significant changes in the Raman spectrum on cycling, the cation-substituted compositions such as $\text{LiMn}_{1.88}\text{Li}_{0.06}\text{Ni}_{0.06}\text{O}_4$ that show good cyclability both at room and elevated temperatures do not exhibit much change in the Raman spectrum on cycling. Clearly, the electrochemical performance is related to some intrinsic materials parameters and further analysis of the Raman spectra is in progress. Also, we have supplied the $\text{LiMn}_{1.85}\text{Li}_{0.075}\text{Ni}_{0.04}\text{Cu}_{0.035}\text{O}_4$ cathode powder to the Lawrence Berkeley National Laboratory for evaluation in lithium ion cells.

In continuation of our investigation of the 5 V spinel cathodes based on $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, we have now examined the lattice parameter differences among the three cubic phases formed during the charge-discharge process with three additional compositions: $\text{LiMn}_{1.42}\text{Ni}_{0.42}\text{Fe}_{0.16}\text{O}_4$, $\text{LiMn}_{1.5}\text{Ni}_{0.42}\text{Mg}_{0.08}\text{O}_4$, and $\text{LiMn}_{1.58}\text{Ni}_{0.42}\text{O}_4$. The data obtained with these compositions also support the plot we presented in our previous report, illustrating an increase in the capacity retention with decreasing lattice parameter difference. Also, the rate capabilities of the 5 V spinel compositions are found to increase as the lattice parameter differences among the three cubic phases decrease. Thus the 4 V and 5 V spinel oxides share a common dependence of the cyclability and rate capability on the lattice parameter differences among the two or three cubic phases formed. Additionally, with an aim to compare the Mn dissolution in the 4 V and 5 V spinel cathodes, we have evaluated the manganese dissolution by (i) soaking the oxide powders in 1 M LiPF_6 ethylene carbonate/diethyl carbonate electrolyte at 55°C for 7 days and (2) after subjecting the coin cells to 20 cycles. The 5 V spinel cathodes also do experience Mn dissolution similar to the 4 V spinel cathodes although the former contains mostly Mn^{4+} while the latter contains significant amount of Mn^{3+} . Moreover, we do not find any clear correlation between the % capacity fade and the amount of Mn dissolution in both the 5 V and 4 V systems.

Reason for changes from original milestones: N/A

BATT TASK 5 DIAGNOSTICS

TASK STATUS REPORT

PI, INSTITUTION: R. Kostecki, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Electrode Surface Layers

SYSTEMS: High-voltage, high-energy: Gr/LiPF₆+EC:DEC/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂,
Low-voltage, high-stability: Gr/LiPF₆+EC:DEC/LiFePO₄,
High-voltage, high-power: Gr/LiBOB+gBL:EA:LiMn₂O₄

BARRIER: Short lithium battery calendar/cycle lifetimes.

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface chemistry, interfacial phenomena, and cell power or capacity decline.

APPROACH: Our approach is to use *in-situ* and *ex-situ* Raman microscopy, scanning probe microscopy (SPM), spectroscopic ellipsometry, scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and standard electrochemical methods to characterize cell components taken from baseline BATT Program cells, fresh electrode materials, and thin-film or single particle model electrodes. Data to be collected include changes in electrode surface morphology, structure, electronic conductivity, electrode surface chemistry, and SEI thickness and composition, all of which accompany cell cycle-life tests.

STATUS OCT. 1, 2004: We expect to develop better understanding of the mechanism of carbon retreat in the composite LiAl_{0.05}Ni_{0.8}Co_{0.15}O₂ cathodes and its impact on the cathodes electrochemical performance upon cycling and storage in LiPF₆-EC-EMC electrolyte at elevated temperatures. We intend to identify and characterize physico-chemical processes, which are responsible for this effect, and establish possible links with other detrimental phenomena. The correlations between electrode history, electrode surface properties, and temperature for baseline LiAl_{0.05}Ni_{0.8}Co_{0.15}O₂ cathodes will be developed. We expect to determine and verify the key elements for high-rate performance of LiFePO₄ composite cathodes i.e., the effect of residual carbon, solid-solution doping by metals supervalent to Li⁺.

EXPECTED STATUS SEPT. 30, 2005: We expect to define relationships between electrochemical performance and limitations of BATT baseline systems and cell history, abuse tolerance, electrodes surface properties and interfacial phenomena. We intend to develop good understanding of the key elements for good electrochemical performance of LiFePO₄ and LiMn₂O₄ and LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ composite cathodes. We anticipate determining the mechanism of graphite disordering in the composite anodes and carbon retreat in the composite cathodes evaluate its impact on long-term Li-ion cell performance. We also expect to develop an experimental methodology to carry out *in-situ* spectroscopy and microscopy exploratory studies of single particle electrodes to characterize BATT baseline electrode materials.

RELEVANT USABC GOALS: 15 year life, 30 ohm-cm² area-specific impedance, 300,000 shallow discharge cycles.

MILESTONES: (a) Quantitative and qualitative analysis of carbon retreat from the composite cathodes by ¹³C distribution examination in model Li-ion cells by March 2005. (b) Preliminary evaluation of *in-situ* microwave-assisted synthesis of graphitic carbon matrix for composite cathodes by June 2005.

PROGRESS TOWARD MILESTONES

Our first objective is to improve high-rate performance of composite cathodes by direct *in-situ* microwave-assisted synthesis of graphitic carbon matrix. We determined that improved electrochemical properties of LiFePO_4 are associated with a larger ratio of sp^2 -coordinated carbon, which exhibits better electronic conductivity than disordered and/or sp^3 -coordinated carbonaceous materials. However, the *in situ* carbon coating of LiFePO_4 by simple pyrolysis of organic precursors at temperatures below 800°C cannot produce graphite-like conductive carbon.

The main advantage of using microwave heating is that the energy is derived directly to the material through molecular interaction with the electromagnetic waves, which reduces treatment time considerably and produces carbons of higher crystallinity, and consequently, better electronic conductivity. To test this concept we carried out a series of preliminary experiments in which we microwaved mixtures of organic precursors and different types of carbon initiators.

A thin film of synthetic graphite SFG-6 and novolak-resin photoresist precursor (1:4 by weight) was spin-coated on a glass substrate and then exposed to microwave radiation at various power levels and for different time periods. Figure 1 shows Raman spectra of two components of the precursor mixture i.e., SFG-6 graphite and photoresist. The photoresist does not display any Raman bands but it produces a strong fluorescent background. Two peaks at ~ 1350 and $\sim 1600\text{ cm}^{-1}$ correspond to the D and G bands of elemental carbon, respectively. The relative intensity of the D band vs. G band is attributed to increased carbon disorder in microcrystalline graphite. Interestingly, microwave treatment of the precursor thin film at 600W for 3 min. that was produced carbon which shows no trace of D band, which indicates a higher level of crystallinity than the original SFG-6 graphite. The microwave synthesized carbon was also found to possess excellent phase purity. As the matter of fact, the observed spectrum is identical to the spectral signature of the highly oriented pyrolyzed graphite (HOPG). Excellent electrical properties can be expected for such a highly graphitic material. We plan on extending this method for the preparation of highly conductive graphite coatings on cathode active material powders and graphites that can be used as active materials in anodes.

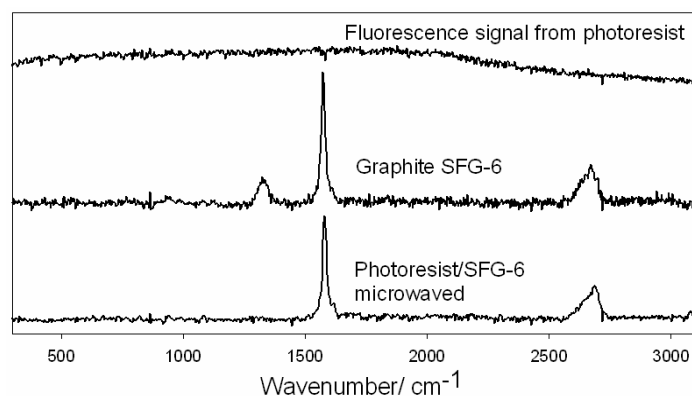


Figure 1. Raman spectra of precursor mixture (SFG-6 graphite + OCG 825-35CS photoresist, 1:4 by weight) and carbon residue after microwave treatment at 600 W for 3 minutes in N_2 atmosphere.

Our second objective is to study in detail the role of carbon additive in composite cathodes and its implications for battery high-rate performance. We continue in-depth diagnostic studies of the mechanism of carbon retreat. In collaboration with Vincent Battaglia (Task 1), ^{13}C enriched composite cathodes are being currently manufactured. Electrochemical calendar life/cycle life tests of cells with ^{13}C -enriched cathodes will be carried out in the coming weeks.

TASK STATUS REPORT

PI, INSTITUTION: W.-S. Yoon and X.-Q. Yang, Brookhaven National Laboratory

TASK TITLE - PROJECT: Diagnostics - Battery Materials: Structure and Characterization

SYSTEMS: High-power Li-ion, high-energy Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to determine the contributions of electrode materials changes, interfacial phenomena, and electrolyte decomposition to cell capacity and power decline. The results of these studies will be used to guide the exploratory research for new cathode, anode, and electrolyte materials for high power lithium batteries.

APPROACH: Our approach is to use a combination of *in situ*, *ex situ* and time resolved synchrotron techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. *Ex situ* soft X-ray absorption spectroscopy (XAS) will be used to distinguish between surface and bulk processes on electrodes using both electron yield (EY) and fluorescence yield (FY) detectors. Time-resolved X-ray diffraction technique will also be used to understand the reactions that occur in charged cathodes at elevated temperatures in the presence of electrolyte. Hard and soft XAS will be used to elucidate the charge compensation mechanisms for cathode materials during electrochemical cycling. This work will be carried out in collaboration with other BATT members.

STATUS OCT. 1, 2004: In FY 2004 comparative studies between Gen2 ($\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) cathode and LiMn_2O_4 spinel cathode have been completed using *in situ* X-ray diffraction (XRD) technique. Both cathodes were cycled at room temperature and 55 °C. We have developed time resolved XRD technique using image plate detector (IPD) and the thermal stability study of cathode materials at elevated temperatures in the presence of electrolyte is ongoing. We have completed the *in situ* hard X-ray XAS and XRD work on $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ electrode. Synchrotron based X-ray studies on the effect of new electrolytes and additives on the stability of LiMn_2O_4 electrodes at elevated temperatures are ongoing.

EXPECTED STATUS SEPT. 30, 2005: We expect to complete the *ex situ* soft X-ray XAS work on $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ electrode during the cycling process. We also expect to complete the *in situ* XRD work on LiFePO_4 during electrochemical cycling at elevated temperatures. *In situ* XRD work on surface-coated LiMn_2O_4 spinel cathode materials will be completed. Soft X-ray XAS using partial electron yield and fluorescence yield detectors will be applied to various cathode materials at the O, F, and P K edges and at the L_3 and L_2 edges of the 3d transition metals.

RELEVANT USABC GOALS: 15 year life, < 20% capacity fade over a 10-year period.

MILESTONES:

- 1) Complete *ex situ* soft X-ray XAS on $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, during cycling. (Apr. 2005)
- 2) Complete *in situ* XRD work on surface-coated LiMn_2O_4 spinel cathode materials. (Oct. 2005)

PROGRESS TOWARD MILESTONES

More *in situ* XRD work on spinel LiMn_2O_4 electrode during cycling at elevated temperatures has been completed. The comparison between the spectra collected from the samples cycled in a conventional $\text{LiPF}_6/\text{EC-DMC}$ electrolyte and a more stable composite $\text{LiPF}_6/\text{EC-DMC}$ electrolyte using 0.1 M tris(pentafluorophenyl) borane (TPFPB) as an additive demonstrated the decomposition of the electrolytes is an important factor for the capacity fading of the spinel cathode materials. This decomposition causes the deposition of contaminants at the surface of electrodes, forms the blockage of Li-ion paths, and resulting in the inactivation of the cathode materials. The spectra collected from the sample which underwent washing procedure with TFPBP added DMC after multiple cycling at elevated temperature showed that the not-reacting parts of the electrode regained its reactivity after washing. Since TFPBP has ability to help dissolving LiF salt into organic solvents, it is reasonable to believe that the major contaminant is LiF.

Soft X-ray (200 to 1000 eV) absorption spectroscopy (XAS) at the O K-edge and the metal L-edges, in both the fluorescence yield (FY) and the partial electron yield (PEY) mode, has been used to probe the electronic structure of electrochemically deintercalated $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$. It is interesting to note the significant differences of Ni L_{II,III}-edge XAS spectra for $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, at various x values, obtained by two different detection mode, the PEY and FY modes. As shown in Fig. 1, the Ni L_{II,III}-edge XAS spectra of $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, obtained in the FY mode appeared at higher energy region compared with those obtained in the PEY mode. Since the PEY and FY probe the surface and bulk respectively, It was concluded that Ni^{2+} ions at the surface are oxidized mostly to Ni^{3+} whereas Ni^{2+} ions in the bulk are oxidized further to Ni^{4+} by comparing the calculated and observed Ni L-edge XAS spectra,. This difference in the electronic structure of Ni ions between the surface and the bulk is more distinguishable in the case of $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$. Our previous soft XAS study on $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ using both the FY and PEY modes clearly showed that Ni ions on the surface of the electrode remain mostly unchanged in the Ni^{2+} oxidation state during charge whereas charge compensation in the bulk is achieved mainly by the oxidation of Ni^{2+} to Ni^{4+} ions. The difference in electronic structures during charge between the surface and bulk is a unique feature of the nickel-based cathode materials. It is observed that the more nickel content in the materials, the more severe difference between the surface and the bulk. Compared to the soft XAS results of $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$, nickel sites of $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ show less difference between the surface and the bulk. This effect could also be attributed to the Co doping.

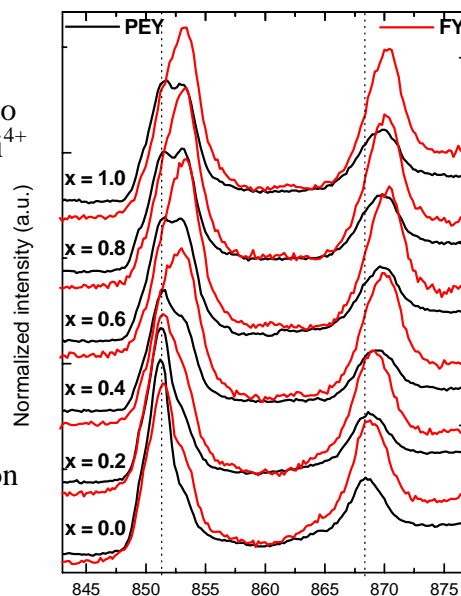


Figure 1. Ni L-edge XAS spectra of $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ during charge.

P K-edge XAS experiments in Fluorescence Yield (FY) mode were performed for $\text{Li}_{1-x}\text{FePO}_4$ electrodes at different x values. Pre-edge peak was not observed in P K-edge XAS spectrum for the pristine LiFePO_4 . Upon Li deintercalation, however, pre-edge peaks start to appear in the lower energy region of main edge. The gradual increase of pre-peak intensities with the Li-ion deintercalation shows that these pre-edge peaks are originated from the hybridization of P 3p states with the Fe 3d states. It is very interesting to notice that such hybridization occurs in spite of the presence of oxygen atoms that separate phosphorus from iron.

TASK STATUS REPORT

PI, INSTITUTION: P.N. Ross, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics – Interfacial and Reactivity Studies

SYSTEMS: High Power Battery

BARRIER: Short battery lifetime

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell failure.

APPROACH: Our approach is to use in-situ Fourier transform infrared (FTIR) spectroscopy to study the *interfacial chemistry* in model electrode/electrolyte systems. The spectrometer optics and spectroelectrochemical cell have a special design that enables any electrode material to be studied. Model systems to be studied this year include new Mn-based cathode materials and new Sb-based anodes. The FTIR spectroscopy will be accompanied by classical electroanalytical methods such as cyclic voltammetry and the rotating ring-disk electrode (RRDE).

STATUS OCT. 1, 2004: The oxidation and reduction chemistry of the new Li-ion battery electrolyte salts, LiBOB has been determined. The oxidative stability of GEN2 Li-ion battery electrolyte with the new Mn-based cathodes materials has been determined. The composition of the SEI layer on Sb-based anodes in PC-based electrolyte is under investigation.

EXPECTED STATUS SEPT. 30, 2005: The composition and stability of the SEI layer on Sb-based anodes in PC-based electrolyte will be known. The predicted advantages of a Sb-based anode vs. carbon/graphite anode for the high power battery application will be established. Irreversible changes to the SEI layer of GEN2 anodes due to cycling at low temperature will be determined.

RELEVANT USABC GOALS: 15-year life, < 20% capacity fade over a 15-year period.

MILESTONES:

- 1) Determine the potential advantages of a Sb-based anode vs. carbon/graphite anode for the high power battery application based on differences in composition and stability of the SEI layer. (May 2005)
- 2) Determine the nature of irreversible changes to the SEI layer of GEN2 anodes due to cycling at low temperature. (Sept. 2005)

PROGRESS TOWARDS MILESTONES

Interfacial Chemistry at Low Temperature

We initiated the study of interfacial chemistry in Li-ion batteries at low temperature. The first experiments have focused on interfacial phenomena observed with GEN2 anodes in different so-called low temperature electrolytes. Of particular interest is the irreversible increase in interfacial impedance in anodes after HPPC cycling at low temperature. Swagelok cells are being used with ex-situ analysis of the anodes using a combination of FTIR and XPS. Some preliminary experiments were done with a low temperature version of GEN2 electrolyte, EC:PC:DMC (1:1:3) with 1 M LiPF₆. A Mag10 anode went through formation cycling at low rate at room temperature (discharge capacity at C/25 was 354 mAh/g) followed by HPPC testing. The cell was then placed in the environmental chamber at – 30 C, subjected to HPPC testing at – 30 C, then returned to room temperature, and tested again at room temperature. The results are shown in the figure. The ASI increases by approximately one order of magnitude at – 30 C for both charge and discharge processes. However, no irreversible loss in capacity or rate capability was observed when the cell was returned to room temperature. The electrode was removed from the cell and examined by FTIR. There was no significant difference observed in the composition of the SEI layer after the HPPC test at – 30 versus room temperature. The irreversible charge consumed during SEI layer formation in this EC-PC electrolyte was somewhat higher than what we normally see with GEN2 electrolyte, and correspondingly the SEI layer did appear by FTIR to be thicker. Otherwise the PC did not seem to be affecting the composition of the SEI layer.

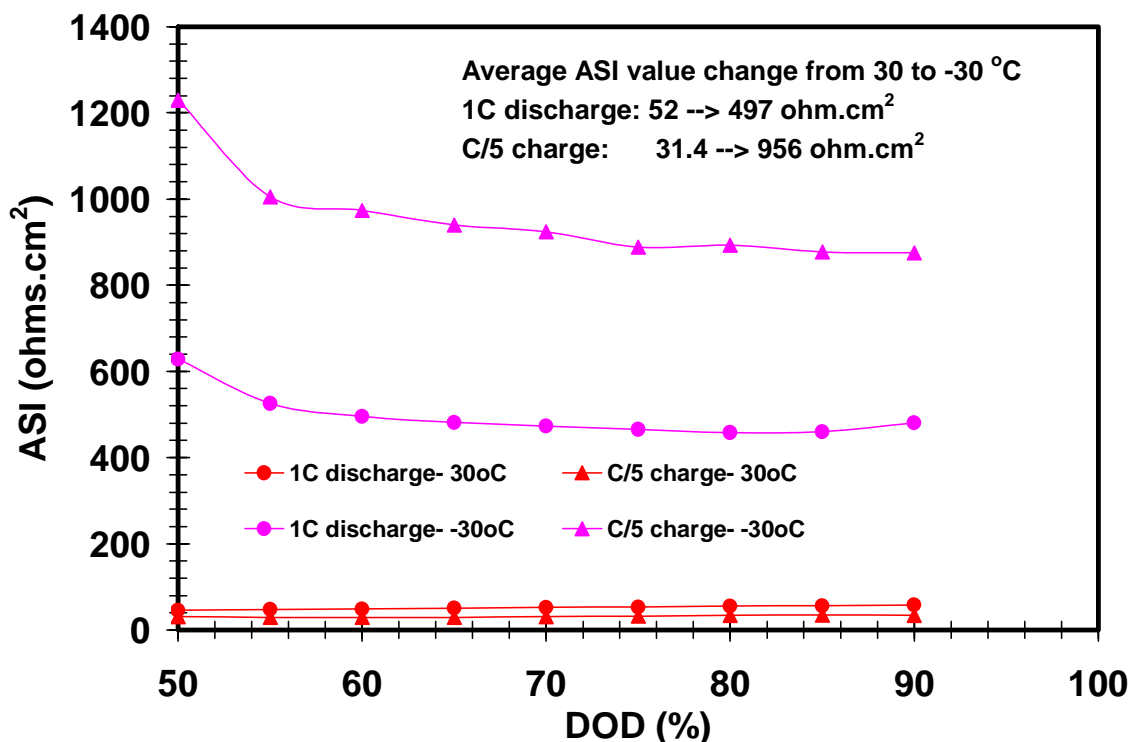


Figure 1. ASI vs. DOD of cells at 30°C and -30°C, evaluated using a HPPC test

TASK STATUS REPORT

PI, INSTITUTION: G. Ceder, Massachusetts Institute of Technology
C. Grey, SUNY at Stony Brook

TASK TITLE - PROJECT: Diagnostics - First-Principles Calculations and NMR Spectroscopy of Cathode Materials

SYSTEMS: Doped lithium nickel manganese oxides; lithium iron phosphates

BARRIERS: Low rate capabilities, high cost, poor stability.

OBJECTIVES: Determine the effect of structure on stability of cathodes. Explore rate limitations and relation to structure.

APPROACH: Use solid state NMR to characterize local and diffraction/TEM for long range structure, as a function of sample preparation method, state of charge and number of charge cycles. Use first principles calculations (density functional theory) to identify redox-active metals, relative stability of different structures, and the effect of structure on cell voltages; and to identify promising cathode materials for BATT applications. Anticipate possible instabilities in materials at high states of charge by using calculations. Use calculations and NMR to identify low activation energy pathways for cation migration and to investigate electronic conductivity.

STATUS OCT. 1, 2004: The analysis of the local and long range structure of $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$ (calculations, diffraction and NMR) will have been completed. NMR studies of local structure of $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$ following extended cycling studies will have been completed.

EXPECTED STATUS SEPT. 30, 2005: Correlations between $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$ local and long range structure and stability will have been completed. Joint NMR/calculations of conduction mechanisms (ionic and electronic) of BATT cathode materials will be underway. Applications of NMR and calculation methodology to other relevant systems under investigation by members of the BATT program will be ongoing.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade

MILESTONES:

- 1) Complete analysis of x-ray and neutron diffraction of $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$. Perform initial tests on conductivity model. (Nov. 1, 2004)
- 2) Complete analysis (NMR, TEM, diffraction) of $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$ as a function of synthesis method. Examined effect of structure on Li^+ mobility in $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$ (calculations/NMR); extension of approach to other BATT systems will be underway. Complete studies of acid-leached $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$ (Thackeray) and Ni^{3+} -doped material (Goodenough). Outlined and performed initial test of stability prediction methodology. (May 1, 2005).

PROGRESS TOWARD MILESTONES

We have finished our analysis of the X-ray diffraction patterns of the series $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$. These patterns show additional peaks between 20 and 35° , 2θ , (Figure 1), which are ascribed to Li_2MnO_3 (i.e., $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$)-like ordering in the transition metal (Ni, Mn and Li) layers. This ordering is rarely perfect, and stacking faults of the layers are observed. These faults result in characteristic broadening and apparent changes in the intensities of the reflections caused by the Li_2MnO_3 -type ordering, making a full analysis of the profiles difficult. We have now completed our study of these faults, by using the program DIFFaX (Figure 2) to model the XRD data. Our results illustrate that Li_2MnO_3 samples that have been heated for 1 day contain approx. 10 % of faults (i.e., a stacking fault on average every 10^{th} $[\text{Li}_{1/3}\text{Mn}_{2/3}]$ layer), while the number of faults drop to only 2% after heating for a month. The $x = 1/2$ and $1/3$ materials contain similar types of stacking faults. Materials can be prepared that show much less order, by using shorter heat treatment temperatures and by quenching from high temperature. Neutron diffraction of the $x = 1/2$ material has been completed. The pair distribution function (PDF) analysis of the data illustrates that Ni shows a strong tendency to occupy sites near Mn in the transition metal layers. This information, coupled with the NMR data for the same sample, was used to generate a model for the local and long-range ordering in this system. This completes the work for the first milestone.

Our detailed structural models from NMR, XRD, ND and TEM, developed as part of this work, coupled with predictions from ab-initio calculations, provide a platform with which to correlate changes in electrochemical performance with structural properties. These studies are now ongoing. The characterization of the Ni^{3+} -excess material (Goodenough) by NMR has been completed. Initial calculations of the polaron localization energy in LiFePO_4 and LiMnPO_4 have been performed and work on a theory for conductivity prediction is progressing.

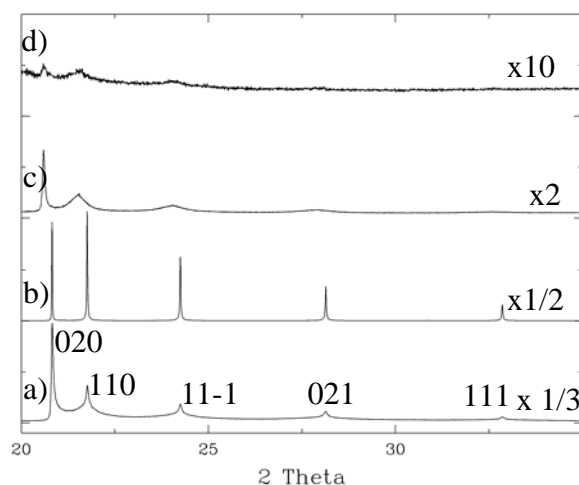


Figure 1. Expansions of the XRD patterns of a) Li_2MnO_3 heated at 850°C for 1 day, b) Li_2MnO_3 heated at 1000°C for 1 month, and c) $\text{Li}(\text{Li}_{1/9}\text{Ni}_{1/3}\text{Mn}_{5/9})\text{O}_2$ (1000°C , 3 days) and d) $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (1000°C for 3 days). The peaks are indexed in the C2/m space group.

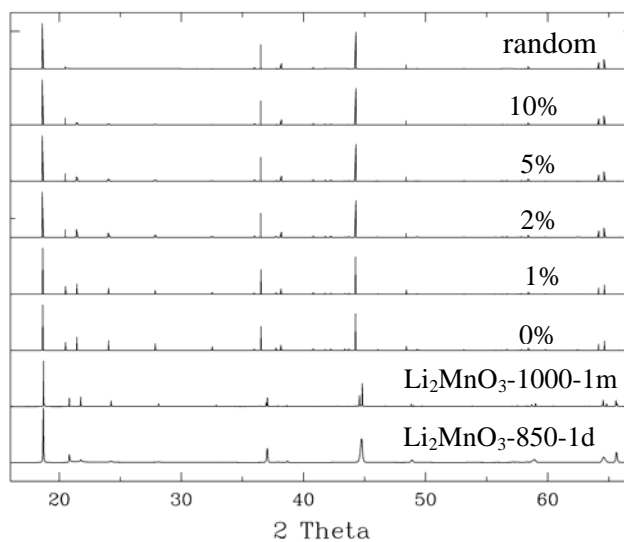


Figure 2. Comparison between experimental and simulated XRD patterns (calculated with DIFFaX) for Li_2MnO_3 , with C2/m stacking and different percentages of stacking faults.

TASK STATUS REPORT

PI, INSTITUTION: T.M. Devine, Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT: Diagnostics – Corrosion of Current Collectors

SYSTEMS: Low-Cost Li-Ion

BARRIERS: Uncertain and possibly inadequate corrosion resistance of Al current collectors

OBJECTIVES: Determine the influence of corrosion and passivation of Al current collectors on the capacity loss of Li-ion batteries. Determine the effect of water contamination of battery electrolytes on the corrosion and passivation of Al current collectors. Compare/contrast the corrosion and passivation of Al in battery electrolytes with salts of LiPF_6 and LiBOB.

APPROACH: The program consists of three tasks, which are worked on in parallel. In Task 1, the influence of corrosion and passivation of Al current collectors on a battery's loss of capacitance is quantitatively evaluated. Three conditions of the Al current collectors are investigated: 1) Al covered with an air-formed film of Al_2O_3 , which is the current collector's surface condition in an unused battery; 2) Al covered with a duplex surface film consisting of an inner layer of air-formed Al_2O_3 and an outer layer of AlF_3 , which is the surface condition that might develop after a number of charge/discharge cycles in LiPF_6 electrolytes; 3) Al covered with a 1- μm thick anodized film of Al_2O_3 , which is a surface condition that earlier work has shown to exhibit excellent corrosion resistance. In all three cases the current collectors are coated with cathodes of LiFePO_4 . In Task 2, concentrations of water ranging from 2 to 100 ppm are deliberately added to battery electrolytes with salts of LiPF_6 and LiBOB to investigate the influence of water contamination on the corrosion and passivation of Al current collectors. In Task 3, electrochemical tests and *in situ* Raman spectroscopy are employed to probe the mechanism of corrosion of Al current collectors. Task 3 provides the mechanistic understanding of the corrosion phenomena that contribute to a battery's loss of capacitance as determined in Task 1.

STATUS OCT. 1, 2004: Aluminum electrodes with anodized films formed in sulfuric acid (to produce 1- μm thick layer of Al_2O_3) and in battery electrolytes (to produce duplex film with outer layer of LiPF_6) will be prepared and coated with cathodes of LiFePO_4 (Task 1). An electrochemical technique, which was proposed by Tobias and colleagues, will be evaluated as a tool for measuring small quantities of water (1-10 ppm) in battery electrolytes containing EC, DMC, and PC as solvent (Task 2). The electrochemical cell for *in situ* Raman spectroscopy of Al in battery electrolytes will be designed and constructed along with optics to direct laser light onto the Al sample and to collect Raman scattered light from the Al sample. (Task 3). Inspection of current collectors from life-tested coin cells will continue with an emphasis on cells that utilized new electrolytes (e.g., salt of LiBOB) (Task 1I).

EXPECTED STATUS SEPT. 30, 2004: The contribution of corrosion of current collectors to a battery's overall loss of capacitance will be quantitatively expressed. The mechanism of passivation of Al and the identity of the passive film of Al will be determined in battery electrolytes that contain LiBOB. The possible role of particular cathodes in causing corrosion of Al current collectors in electrolytes with LiPF_6 and LiBOB will be identified. The likelihood of corrosion of Al current collectors in LiBOB electrolytes will be compared to the susceptibility of Al current collectors to corrosion in LiPF_6 electrolytes.

RELEVANT USABC GOALS: 10 year life; < 20% capacity fade.

MILESTONES: 1) Determine influence of water contamination on the resistance of cathode-coated Al to corrosion in battery electrolytes with salts of LiPF_6 and LiBOB. (8/05). 2) Determine relevance of A's susceptibility to corrosion on a battery's loss of capacitance. (8/05)

PROGRESS TOWARD MILESTONES

The current research was focused on three aspects of the corrosion behavior of aluminum in an electrolyte consisting of LiBOB dissolved in 1:1 ethylene carbonate (EC) and dimethyl carbonate (DMC).

(1) Corrosion of Aluminum in salt-free organic solvent (1:1 EC+DMC)

Aluminum foil was polarized in 1:1 EC+DMC from the open circuit potential (OCP) to 6V vs. Li. Above a critical potential, aluminum sustained significant pitting corrosion. The cause of pitting corrosion in EC+DMC is unclear, and may be related to contaminant(s) in the solvent. In any event, a protective film is not formed on aluminum in salt-free EC+DMC so the air-formed surface oxide controls aluminum's corrosion behavior. Aluminum's air-formed oxide cannot prevent pitting corrosion at high potentials in salt-free EC+DMC.

(2) Passivation of aluminum in 1M LiBOB/EC+DMC

Cyclic voltammograms (CV), in which the potential was swept to maximum values of 4.5, 5.5, and 6.5V, were obtained for aluminum in 1.0 M LiBOB/EC+DMC. Even when the potential reached 6.5 V, no corrosion was detected on the surface of aluminum. The combined results of CV, electrochemical impedance spectroscopy (EIS), and electrochemical quartz crystal microbalance (EQCM) measurements indicate a passive film is formed on aluminum anodically polarized in 1.0 M LiBOB/EC+DMC and the film's thickness increases with increasing potential. Specifically, (i) CV curves exhibited a pronounced hysteresis, (ii) capacitances, as measured by EIS (see Table I), decreased with increasing potential, and (iii) aluminum's mass, as measured by EQCM, increased with increasing potential.

(3) Passivation of aluminum in electrolytes of LiBOB + LiTFSI

Battery electrolytes with the salt lithium trifluorosulfonimide (LiTFSI) exhibit excellent performance characteristics, except for their severe corrosivity towards aluminum. Corrosion pits formed on the surface of aluminum after 3 cycles of CV from OCP to 5.5V in 1.0 M LiTFSI/EC+DMC. Pits with diameters as large as 20 μm are widely distributed on the surface of aluminum. LiBOB was found to either markedly reduce, or, in some instances, to completely eliminate the corrosion of aluminum by LiTFSI. The passive film formed on aluminum by three CVs in 1M LiBOB was able to protect aluminum against significant corrosion when subsequently polarized in 1M LiTFSI. Aluminum subjected to 3 CVs (maximum potential of 5.5V) in electrolytes composed of a mixture of LiTFSI and LiBOB with as little as 2% LiBOB, which was the smallest concentration tested, were free of any detectable corrosion. Based on the results of EIS and high-resolution microscopy, the passivation layer formed on aluminum's surface in LiBOB efficiently protects against corrosion by LiTFSI.

Table 1. The capacitance of aluminum after CV measurement

Condition	Before CV	4.5V	5.5 V	6.5 V
CPE($\mu\text{F}/\text{cm}^2$)	2.64	2.76	2.27	1.98

BATT TASK 6 MODELING

TASK STATUS REPORT

PI, INSTITUTION:J. Newman, Lawrence Berkeley National Laboratory

TASK TITLE – PROJECT:Improved Electrochemical Models

SYSTEMS:

High-voltage, high-energy: Gr/LiPF₆+EC:DEC/LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂

Low-voltage, high-stability: Gr/LiPF₆+EC:DEC/LiFePO₄

High-voltage, high-power: Gr/LiBOB+ γ BL:EA/LiMn₂O₄

BARRIERS:Poor transport properties, capacity and power fade

OBJECTIVES:Develop experimental methods for measuring transport and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

APPROACH:Use simulations to improve understanding of the SEI layer and particle volume expansion. Develop improved experimental methods for measuring transference numbers in liquid electrolytes.

STATUS OCT. 1, 2004:Modeling of dendrite growth is complete. A stability analysis that determines practical conditions under which dendrite growth can be inhibited or eliminated by mechanical means is complete. Comparison of SEI simulations with experimental results and refinement of the model is ongoing. Full characterization of transport in LiPF₆ electrolytes is ongoing.

EXPECTED STATUS SEPT. 30, 2005: Work will continue on a model for calculating stress distributions in electrode materials during intercalation. Full characterization of transport in LiPF₆ electrolytes will be ongoing. New projects may start either on active material connected to a current collector and/or on including the Ni-MH system on the dualfoil model platform with side reactions.

RELEVANT USABC GOALS: 30 ohm-cm² area-specific impedance, cold cranking capability to -30°C, 300,000 shallow discharge cycles, abuse tolerance to cell overcharge and short circuit

MILESTONES: Model for calculating stress distributions in electrode materials during intercalation will be completed. (Dec. 2004)

PROGRESS TOWARD MILESTONES

Particle Expansion and Fracture

We have formulated a mathematical model of particle volume expansion, which is used to calculate stress profiles in active electrode material due to lithium insertion. Results indicate that graphite particles will possibly fracture at high charge rates typical of hybrid-electric vehicle applications, but are unlikely to fracture at low to moderate rates. Refinements to the model include the influence of nonidealities in the solid solution upon the electrode kinetics and thermodynamic factor, both of which influence the stress that is generated in the particle. Lithium insertion and extraction under potentiostatic and galvanostatic conditions have been successfully simulated with the model. The volume-expansion model has been completed and we are in the process of writing up the results.

Transport Property Measurement

The development of an anion-reversible electrode has continued for LiPF_6 electrolytes of interest. This reference electrode will be used in EMF measurements in order to determine activity coefficients independently. These measurements will enable a more accurate determination of the transference number as a function of electrolyte concentration in these systems. Transference number measurements, when combined with remaining transport property data, will allow for comparison between different electrolytic solutions.

TASK STATUS REPORT

PI, INSTITUTION: V. Srinivasan and J. Newman, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling - Modeling of BATT Program Baseline Chemistries

SYSTEMS: LiFePO_4 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and LiMn_2O_4

BARRIERS: Low power capability; capacity/power fade; poor low-temperature operation

OBJECTIVES: 1. Evaluate performance of the three baselines under HEV operation; identify the limiting mechanism in each chemistry. 2. Understand limitations of baselines when operating below room-temperature. 3. Investigate degradation mechanisms and begin development of a cycle-life model.

APPROACH: Develop mathematical models for the BATT baselines. Perform experiments to complement models and extract unknown parameters. Optimize models to satisfy the EV and HEV goals, and use them to compare the baselines to each other. Perform experiments at lower temperatures and use model to understand the limiting processes. Incorporate life-limiting mechanisms into the models.

STATUS OCT. 1, 2004: Models for all three baselines have been complete and the performance limitations identified. A theoretical comparison of the three over a wide discharge range was ongoing.

EXPECTED STATUS SEPT. 30, 2005: Modeling of the baselines for HEV applications and optimization studies will be complete. Experimental measurement of kinetic and transport properties at lower temperatures (<RT) will be ongoing. Modeling of low-temperature operation will be ongoing.

RELEVANT USABC GOALS: $\text{ASI} = 30 \text{ } \Omega\text{-cm}^2$, Cold cranking capability to -30°C ; 300,000 shallow discharge cycles

MILESTONES:

1. Compare the three baselines under full discharge-time range. (Dec. 2004)
2. Identify the best baseline and the optimal design for HEV applications. (Aug. 2005)

PROGRESS TOWARDS MILESTONES

LiFePO₄ baseline: We have started on the simulations of HEV operation on this baseline. In order to predict the ASI on regeneration, it was felt that a better description of charge behavior is needed in the model. Evidence exist that the conductivity of LiFePO₄ is different from that of FePO₄. This difference should translate into a difference in the ASI of the cells between discharge and regeneration. We are now collecting experimental data on charge on half-cells. We will use this data along with the model to understand more about the difference between charge and discharge in this system.

LiMn₂O₄ baseline: In the 3rd quarter of FY04 we had reported model-experimental comparisons of the spinel baseline and had concluded that a contact resistance between the electrode and the current collector was limiting performance. We have since been working with the cell development group to try to implement the use of a carbon-coated current collector to minimize this resistance. The new electrode was tested by cycling at various current densities and the results showed a significant improvement in performance. We will be repeating the experiments to confirm the results and will use this data for the modeling purposes to perform the optimization at various discharge times. Hence the milestone scheduled for Dec 2004 has been postponed to the next quarter.

LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ Baseline: In the previous quarter we had undertaken an extensive model-experimental comparison of this chemistry involving two different cell designs and charging to two different voltages. This study allowed us to establish that a contact resistance (similar to one shown in the spinel system) was giving rise to ohmic drops. The cell development group has since fabricated an electrode on a carbon-coated current collector. We are currently testing these cells.

TASK STATUS REPORT

PI, INSTITUTION: A.M. Sastry, University of Michigan

TASK TITLE - PROJECT: Modeling – Scale-Bridging Simulations of Active Materials in Li-ion Batteries, and Validation in BATT Electrodes

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: Determine superior composition and processing conditions of electrodes for conductivity enhancement, especially for the LiFePO_4 cathode. Develop scale-bridging simulations which will allow identification of the best particle morphologies for both energy- and power-dense systems. Develop superior anodes and cathodes by altering the content and morphologies of conductive materials.

APPROACH: Using new simulations developed to model conductivity of the particle networks within both anodes and cathodes, we will expand our investigations with three major new thrusts: 1) development of scale-bridging models to determine likely electrochemical performance of cathode materials, taking direct account of the effects of particle shape and connectivity; 2) determination of the effect of mechanical compression on real batteries, accounting for both multiple layers and cell compression, and 3) extensive experimental and numerical simulation of conduction in new materials synthesized by other BATT workers (Striebel, Zaghib, Wheeler), and provision of guidance concerning the best morphologies to use.

STATUS OCT. 1, 2004: Experiments (LBNL and UM) and simulations on conduction and electrochemical performance in baseline anodes and cathodes, with correlations developed relating material composition, SEI layer formation and cell capacity losses will be completed. Modeling of other BATT Program baseline chemistries will be ongoing.

EXPECTED STATUS SEPT. 30, 2005: Correlation of cathode performance with particle morphology, including fiber additives will be made. Completion of conductivity and mechanical experiments to quantify losses under realistic loads will be made.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade

MILESTONES:

- 1) Provision of codes for numerical estimates of conductivity with a wide range of fibrous additives to other BATT workers. (Dec. 2004)
- 2) Development of full, finite element simulations of deformation of carbon additives under realistic loads will be completed. (Jan. 2005)
- 3) Implementation of algorithms to allow correlation of particle shape and size with electrochemical performance in Li-ion cells. (June 2005)
- 4) Experimental testing and numerical prediction of the effect of fibrous carbons on conductivity in LiFePO_4 cathodes (with materials from Battaglia, Zaghib, Wheeler). (June 2005)

PROGRESS TOWARD MILESTONES

• Accomplishment toward milestone over last quarter

Last quarter, we stated our plans to extend our previous stochastic model to incorporate microscale dynamics models with the following goals in mind:

1. Map the effects of morphology of electrode on transport mechanisms within a cell, to provide a guidance in selecting particle size and manufacturing processes;
2. Map the effects of conductive additives on the transport mechanism within a cell, to provide guidance for optimizing amounts of additives required for improvement of high-rate performance without sacrificing the energy density; and
3. Simulate distribution of potential and current density within each electrode, to inform estimation of reaction rate.

In this quarter, we have surveyed the relevant literature on several different mechanisms: ionic transport in solid and electrolyte, electron transport in solid particles, and side reactions. We have identified elements of our mathematical model that will incorporate fluid dynamics, thermodynamics and detailed morphological information informing simulation of batteries. Preliminarily, we have investigated molecular, continuum and combined approaches.

We have arrived at a plan for using a combination of molecular and continuum modeling. Our approach will involve both finite element (FE) and computational fluid dynamics (CFD) approached. Instead of application of a stricter form of molecular dynamics (MD) calculations, involving, for example, force-bias Monte Carlo, Brownian dynamics, or Langevin dynamics, we will take a stochastic approach in determining molecular trajectories. The strengths of this approach are the relative ease by which several commercial packages will be incorporated, and the reduced computational effort expected, over an MD approach.

• Further plans to meet or exceed milestone

We will continue developing the mathematical model for analysis of baseline materials, and plan to integrate with other DOE workers as validation of models, and in order to continue to provide guidance on selection/design of materials.

• Reason for changes from original milestone: N/A

PROPOSALS UNDER REVIEW

ORGANIZATION (<i>Principal Investigator</i>)	TITLE	STATUS
Carnegie Mellon University (<i>P. Kumta</i>)	High Capacity, Reversible Encapsulated Porous Nanocomposite Anodes for Lithium-Ion Batteries	Unsolicited Proposal-Under Review
Bar-Ilan University (<i>D. Aurbach</i>)	Development and Study of the High Temperature Performance of Li-Ion Batteries for EV Application	Unsolicited Proposal-Under Review
Michigan Technological University (<i>B. Cornilsen et al.</i>)	Characterization of the cathode structures and nonstoichiometry to improve properties of the Mn-containing, Li-ion, Baseline Cathodes	Unsolicited Proposal-Under Review
Massachusetts Institute of Technology (<i>Y. Shao-Horn</i>)	TEM and AFM studies of nanoparticle coating on lithium battery materials: its effect on electrode stability, battery cycle life and battery safety	Unsolicited Proposal-Under Review
University of South Carolina (<i>J. Weidner</i>)	Advanced analysis of electrochemical impedance spectra to measure transport properties in Li-ion batteries	Unsolicited Proposal-Under Review
Graz University of Technology (<i>M. Winter</i>)	Investigations on safety and performance of intermetallic anodes of the BATT program in organic electrolytes by <i>on-line</i> mass spectrometry	Unsolicited Proposal-Under Review

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT) CALENDAR OF RECENT AND UPCOMING EVENTS

October 2004

- 3 - 8 206th Electrochemical Society Meeting – Honolulu, HI (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)

May 2005

- 15 - 20 207th Electrochemical Society Meeting – Quebec City, Canada (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)
- 22 - 27 Lithium Battery Discussion Meeting, LiBD2004 – Arcachon France (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; email: Josh.Thomas@mkem.uu.se; <http://www.icmcb.u-bordeaux.fr/libd>)

June 2005

- 12 - 17 2nd International Conference on Polymer Batteries and Fuel Cells – Las Vegas, NV (Broddarp of Nevada, Inc. and The Electrochemical Society, 792-897-3027, dbrodd@broddarp.com) Riviera Hotel and Casino
- 13 - 17 5th International Advanced Automotive Battery Conference (AABC-05) on VRLA for Traction Applications, and International Symposium on Large Lithium Battery Technology and Application (LLIBTA) – Honolulu HI (Menahem Anderman, Conf. Chair; <http://www.advancedautobat.com>) Sheraton Waikiki Beach Resort

September 2005

- 25 - 30 56th Annual Meeting of the International Society of Electrochemistry – Busan, Korea (Contact: H Kim; hasuckim@plaza.snu.ac.kr)

October 2005

- 16 - 21 208th Electrochemical Society Meeting – Los Angeles, CA (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)

May 2006

- 7 - 12 209th Electrochemical Society Meeting – Denver, CO (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)
- 23 - 29 Lithium Battery Discussion Meeting, LiBD2004 – Arcachon France (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; email: Josh.Thomas@mkem.uu.se; <http://www.icmcb.u-bordeaux.fr/libd>)

October 2006

- 29 - Nov. 3 210th Electrochemical Society Meeting – Cancun, Mexico (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)